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THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM SEMIANNUAL REPORT (April 1977 - September 1977)

T. T. Bramlette, R. W. Mar

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115 and Livermore, California 94550 for the United States Department of Energy under Contract AT (29-1)-789.

Printed March 1978

Sandia Laboratories
energy report

SF 2900-QQB(3-74)

Issued by Sandia Laboratories, operated for the United States Department of Energy by Sandia Corporation.

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $5.50; Microfiche $3.00

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Compiled by

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ABSTRACT

This document summarizes the progress made by the Thermochemical Energy Storage and Transport (TEST) Program in the period April 1977 - September 1977.

ACKNOWLEDGMENTS

The contributions of the following individuals to the TEST Program were essential for its successful functioning, and are acknowledged gratefully:

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THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT PROGRAM SEMIANNUAL REPORT

INTRODUCTION

TEST Program Scope

The Chemical and Thermal Storage Branch of the United States Department of Energy (DOE), Office of Energy Technology, Division of Energy Storage Systems has implemented a National Thermal Energy Storage (TES) Program. The objective of this National Program is to develop and disseminate thermal and thermochemical energy storage and transport technology which offers the potential for energy conservation or fuel substitution (nuclear, coal, or solar for petroleum). The National Program, under the direction of C. J. Swet, consists of three subprograms:

1. Low-Temperature Thermal Energy Storage Program (managed by Oak Ridge National Laboratories) - The objective is to develop sensible and latent heat technologies for low-temperature ($\leqq$ 250°C) applications.

2. High-Temperature Thermal Energy Storage Program (managed by NASA Lewis Research Center) - The objective is to develop sensible and latent heat technologies for high-temperature (250°C) applications.

3. Thermochemical Energy Storage and Transport (TEST) Program (managed by Sandia Laboratories, Livermore) - The objective is to develop reversible chemical reaction technologies for thermal energy storage and transport applications.

Of the three subprograms, the technology is least advanced for thermochemical energy storage and transport. Without exception, no one reaction is understood well enough to allow a commercial scale system to be designed and fabricated. Thus, the current phase of the TEST program is concerned with the development of a technology base from which such systems could be evolved.

The motivation for conducting this research is that thermochemical reactions offer some unique characteristics when compared with sensible or latent heat systems. These include:

- High Energy Densities - Thermochemical storage systems have energy storage densities (based on mass or volume) ranging from about a factor of two to more than an order of magnitude greater than is possible with sensible and latent systems.

- Ambient Storage - Energy storage at ambient temperatures is possible for thermochemical systems, i.e., chemical reactants and products can be cooled to and stored at ambient temperatures. The ability to store at ambient temperatures and still discharge at high temperatures has obvious advantages: chemical interactions between the media and storage container materials are reduced, insulation requirements are eliminated, overall system heat losses are reduced, and potential environmental impact problems (i.e., storing copious quantities of hot material) are avoided.

- Long-Term Storage - With ambient storage, long-term storage with little or no degradation is possible, which makes seasonal or extended storage applications feasible.

- Transportability - Chemical reactions can be selected such that the products and reactants are easily transported, e.g., as gases in a pipeline. Therefore, the endothermic and exothermic reactors can be physically separated by long distances.

- Low Energy-Capacity-Related Costs - The cost of an energy storage system can generally be divided into two categories: power costs and capacity costs. The power related costs are those associated with reactors, heat exchangers, etc.; capacity related costs are associated with raw materials costs, storage tank costs, etc., and are generally low for thermochemical systems.

While these characteristics may be considered advantages for many applications, they must be weighed against the following potential drawbacks:

- Furthest From State-of-the-Art - Thermochemical technologies are the least developed, and considerable amounts of time, money, and effort are required to develop thermochemical systems to commercialization.

- System Complexity - Thermochemical systems probably will be quite complex when compared to sensible and latent heat systems. Not only will individual components be complex, but interactions between various components will be needed to achieve acceptable total system efficiencies.

TEST Program Objectives

To exploit the potential advantages and quantify the disadvantages of thermochemical reactions for energy storage and transport applications, the program has been structured initially to explore a wide range of chemical reactions and applications. In general, the development procedure consists of:

- Identification and evaluation of preferred current and future users of reversible chemical reactions for energy storage and transport.
- Identification of specification requirements and evaluation of available technology and technology needs for selected storage and transport systems.
- Formulation and evaluation of energy storage and transport concepts which meet the requirements established above.
- Definition and development of the required technology.
- Comparison of thermochemical storage and transport concepts with competing technologies, and assessment of their conservation potential.
- Development of the most promising concepts and systems to the point of demonstration on a scale commensurate with commercial application.

It should be emphasized that before a concept is allowed to proceed to the last stage of development, the need for and value of the concept must be established clearly.

The specific applications and concepts currently being addressed in the Program are:

- Thermal Energy Storage (TES) in electric power generating facilities
- TES for solar thermal power systems
- Open-ended methane based chemical heat pipes
- High-temperature chemical heat pipes

• Low-temperature chemical heat pipes

• Solar chemical heat pump storage systems

This list of specific applications is by no means all inclusive. Other applications may surface as the Program progresses, or some of the applications of current interest may not prove feasible. The extent to which these specific applications and concepts apply to general application sectors (i.e., buildings, industry, and utilities) is illustrated in Figure 1. The indicated numbers refer to specific subcontracted programs discussed in a later section of this report.

Program goals have been established assuming at least one thermochemical storage or transport system will be developed for each application. The long-range program goals, milestones, and target dates selected for each application are given in Figure 2. This scheduling has been established on the assumption that all of the applications shown are and will remain of equal importance with regard to potential impact on energy conservation. However, as the thermochemical technologies are developed in this program, it is anticipated that several key applications will become the foci of this program.

General Application Areas Supported By TEST Program / Specific Applications Addressed in TEST Program		Building		Industry		Utilities	
		Solar Heat/Cool	Other Heat	Source of Proc. Heat	Waste Heat Recovery	Solar	Non-Solar
Thermal Energy Storage	TES in electric power generation facilities						4.4**
	TES for solar thermal electric systems*					1.1.1, 1.1.2 1.1.4, 1.1.5 1.1.6	
Chemical Heat Pipe	Open-ended methane-based chemical heat pipe		2.1.1	2.1.1			
	High-temperature chemical heat pipe		2.2.1 2.2.2 2.2.3 2.2.4	2.2.1, 2.2.2 2.2.3, 2.2.4			
	Low-temperature chemical heat pipe		2.2.1	2.2.1			
Chemical Heat Pump Storage	Solar chemical heat pump storage	3.1.1, 3.1.2 3.1.3					

*Includes TES for extended and seasonal storage
**Prior to redirection

Figure 1. A Comparison of General Application Areas (Program Objectives) and Specific Applications Currently Addressed in the TEST Program. Individual Project Identifiers are Used (see Table I)

Technology Concept	Application	Milestone Schedules							Notes
		FY77	FY78	FY79	FY80	FY81	FY82	FY83	
Chemical Heat Pump Storage	Solar Chemical Heat Pump Storage	(△1)		△2	△3	△4			△1 Preliminary Technical and Economic Feasibility Established
Thermal Energy Storage	TES in Electric Power Generating Facilities			△1		△2	△3	△4	△2 Technology Development Complete
	TES for Solar Thermal Power Systems		△1		△2		△3	△4	△3 Prototype Designed, Fabricated, and Checked Out
Chemical Heat Pipe	Open End Methane-Based Heat Pipe		△1			△2		△3	△4 Performance Tests Complete and Analyzed
	High Temperature Heat Pipe (1)	(△1)			△2				◯ Denotes Achievement of Goal
	Low Temperature Heat Pipe (1)	(△1)			△2		△3	△4	(1) Concepts Which Apply to Several Potential Applications, Include Industrial Process Heat, District Heat, and Transmission in Distributed Solar Systems

Figure 2. Thermochemical Energy Storage and Transport Program Goals

STATE-OF-THE-ART ASSESSMENT

The technical disciplines essential to the development of energy storage systems are given in Figure 3. Also listed are probable problem areas in each of these technical disciplines which are generally unresolved at this time, and which must be solved if a thermochemical storage concept is to be developed successfully. A general discussion of the state-of-the-art of these technical disciplines is given below to put thermochemical storage in proper perspective relative to sensible and latent heat systems. More detailed discussions for specific programs are deferred until later.

Chemistry - The heart of a thermochemical energy storage system is the reversible chemical reaction. Without exception, no reaction is well enough researched and understood to allow its immediate incorporation into a storage system. Consequently, a considerable amount of research and development is required to characterize any potentially useful reaction with respect to such parameters as reaction rates, side reactions, reversibility, cyclability, long-term performance, reproducibility, reliability, and impurity effects. For catalyzed reactions, additional questions must be addressed concerning catalyst lifetime, degradation, and poisoning.

Heat Transfer - Equally important to the thermochemical energy storage system are the chemical reactors and process stream heat exchangers. Generally speaking, design techniques are available for predicting system performance. What is lacking, however, is information on the thermophysical and transport properties of the various constituents of the chemical system, catalyst performance, reaction kinetics, and the effects of long-term cyclic operation. Small-scale experiments are required to verify theoretical predictions before large-scale systems are designed and constructed.

Materials - Material compatibility and corrosion problems can be significant depending upon the temperatures of the storage operation and the chemicals involved. Ambient storage mitigates the material problems to the extent that the corrosive conditions may be confined to a fairly small portion of the total system. Unfortunately, the highest temperatures (and therefore the most corrosive environment) are generally found in the reactor and heat exchanger, which generally are the most complex and expensive components of the system.

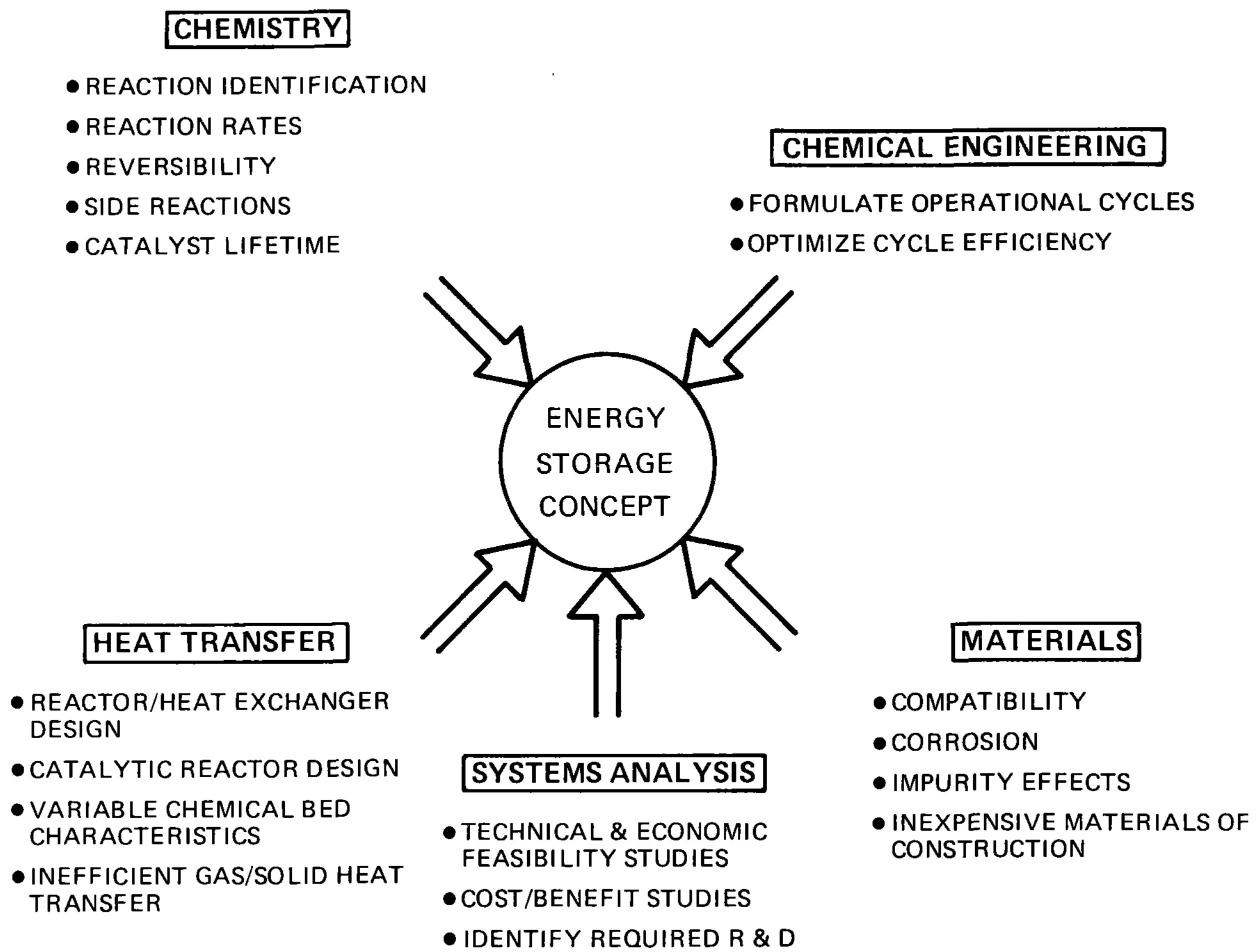


Figure 3. Technical Disciplines Necessary to the Development of Energy Storage Systems

Chemical Engineering - Almost all thermochemical reaction cycles for storage or transport applications contain steps which are potentially wasteful of energy; the net result is a much reduced effective energy density. As an example, consider the reaction

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

which has an attractively large heat of reaction of 380 cal/gm. However, if one considers the fact that 142 cal/gm are lost due to the condensation of H_2O and the sensible heats associated with H_2O and CaO, the net energy density is only 238 cal/gm. The solution, of course, is to use the heat of condensation and sensible heats for secondary purposes; therein lies one of the technical challenges that must be met if the thermochemical system is to be used to its best advantage - operational cycles must be optimized. The recovery and re-use of potential rejected energies are necessities for development of economically viable thermochemical energy storage and transport systems.

Systems Analysis - In addition to the fundamental investigations described above, systems analyses also must be performed. These studies are required to establish the technical and economic feasibility of a proposed concept, to identify required research, and to establish the relative merits of the proposed system when compared with competing technologies. For the programs under consideration, preliminary analyses have been performed; these studies must continue throughout the development process in order to factor in new information as it becomes available and to ensure that the concepts being developed will be technically and economically viable.

In summary, thermochemical technology is at a very early stage of development, and much technology development is needed in each of the five technical disciplines shown on Figure 3 before one can accurately assess the potential of thermochemical techniques, let alone develop thermochemical-based concepts to the point of commercialization.

CURRENT PROJECT GOALS

The long-range TEST Program goals were alluded to briefly in the Introduction. The purpose of the present section is: (1) to provide additional details regarding the long-range program, (2) to show how the FY77 program is related to the long-range program, and (3) to indicate the specific goals of the various projects which comprise the FY77 program.

Five-Year Program

The TEST Program has been divided into four Technical Breakdown Structure elements (see Figure 4): (1) thermal energy storage, (2) chemical heat pipe, (3) chemical heat pump storage, and (4) generic research. Each major element has been further divided into subelements that represent specific concepts/applications being pursued in this program.

The use of thermochemical storage technology in solar thermal electric systems is of interest, with particular attention given to the long duration storage capabilities. The role of thermochemical technology in non-solar utilities is also being addressed. Chemical heat pipes for the transmission of thermal energy for industrial process heat and district heat applications appear to hold significant promise. The current TEST Program is investigating this application in connection with three potential energy sources: (1) a coal gasification plant (open loop heat pipe), (2) a very high temperature nuclear reactor (high temperature heat pipe), and (3) moderate temperature sources available in the United States including nuclear, solar, and fossil (low temperature heat pipe). In addition, the use of chemical heat pipes for transmission in distributed solar systems is also being addressed. The only application of current interest for chemical heat pump storage technology is solar heating and cooling.

The various activities which comprise the long-range TEST Program are given in Figures 5 through 11 for each of the Technical Breakdown Structure subelements. These activities are presented in the form of network diagrams which illustrate the interactions required between various projects if the concept/application is to be successfully developed. Interactions between activities are depicted by nodes; the nodes are indicative of "decision to proceed" points or "technical information exchange" points,

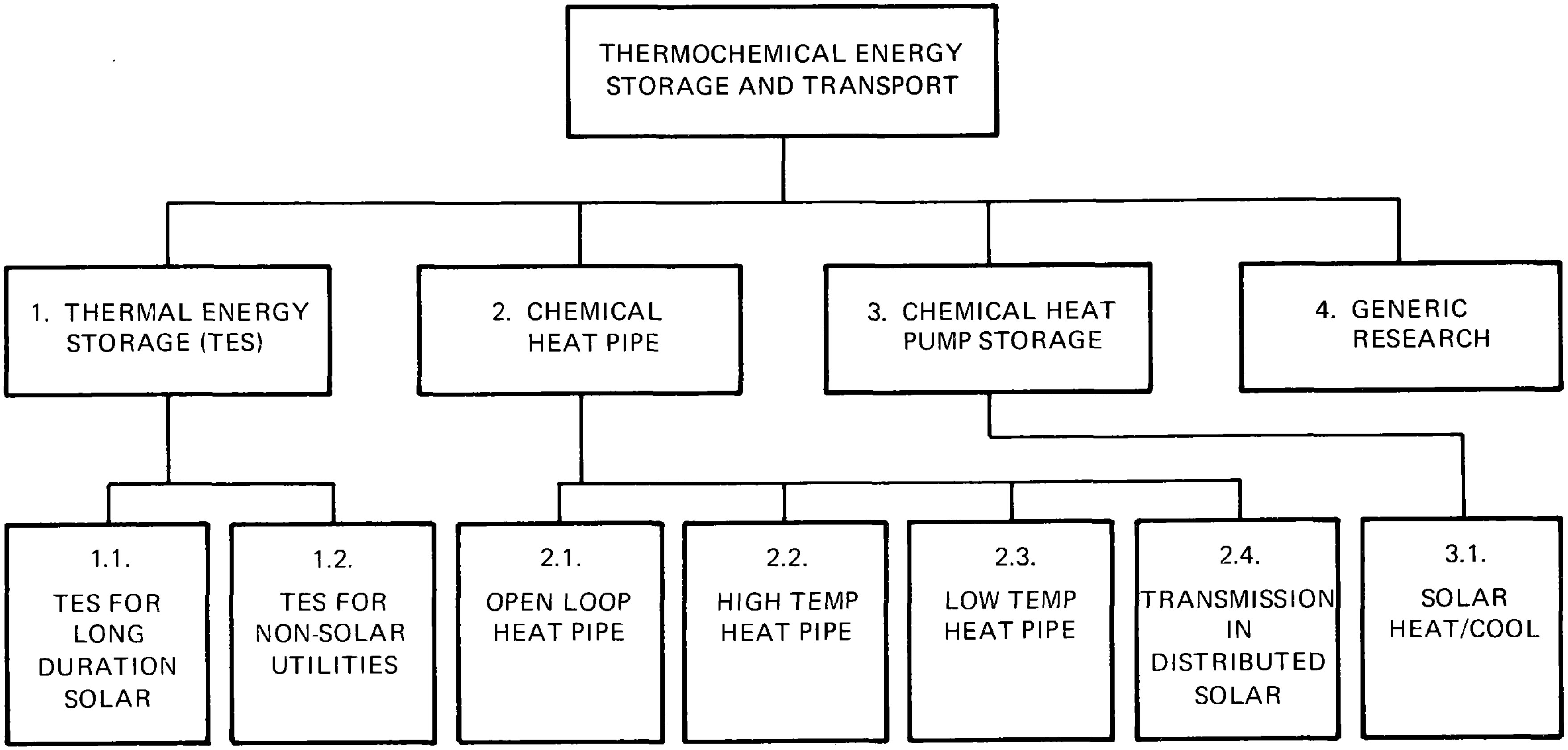


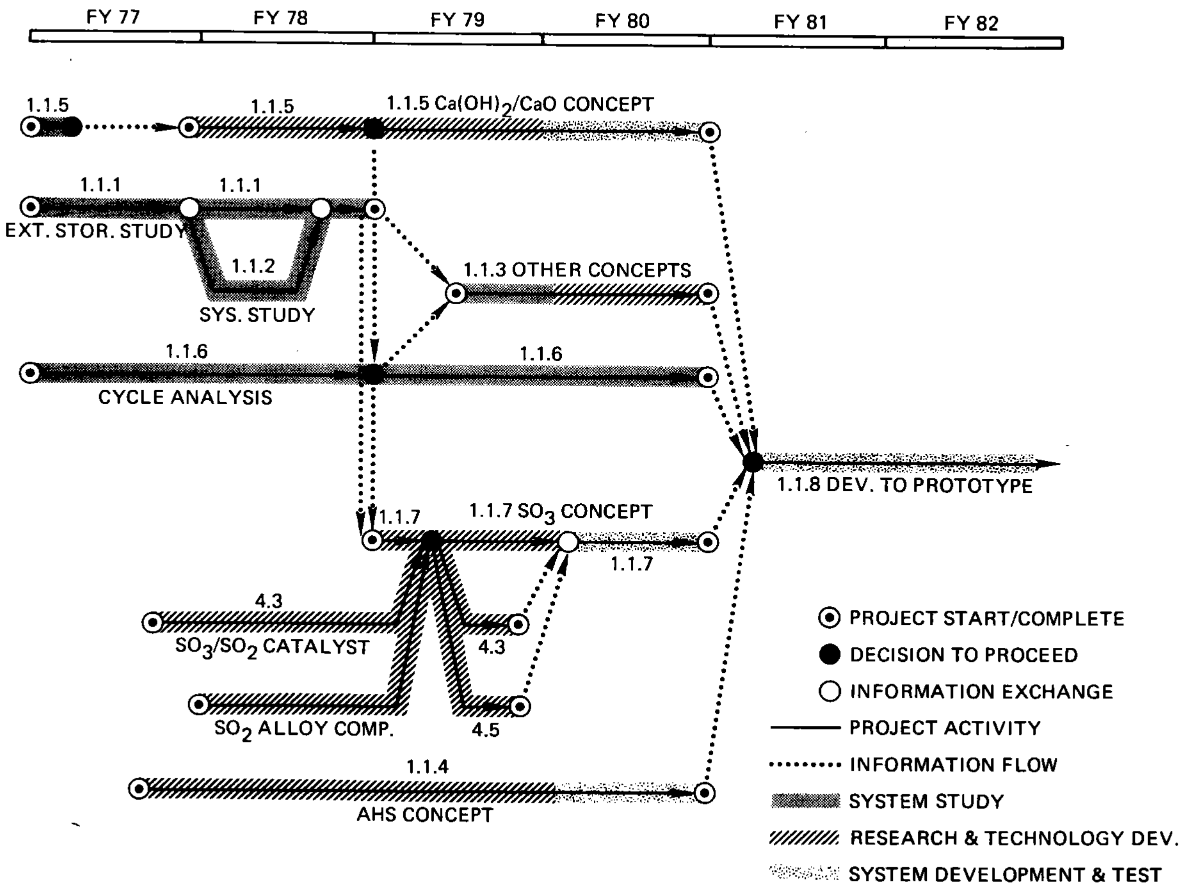
Figure 4. Technology Breakdown Structure for the TEST Program

although continual information flow between all activities is assumed. Also presented is a brief description of the various activities. The project numbers for those activities which are in progress are underlined.

FY 77 Projects

The projects which comprise the FY 77 program and specific goals for each are listed in Table I. The organization is by Technology Breakdown Structure. Also indicated is the current status of each of the goals.

The TEST Program has also been divided into major elements of work, as shown by the Work Breakdown Structure in Figure 12. The Work Breakdown Structure is useful in that it defines the nature of the work performed, and therefore reflects the stage of development of the concept. Generally, as a concept is being developed, the work emphasis varies from system studies to research and technology development to system development and test. The projects comprising the FY 77 Program are categorized in Figure 13, by both Technical Breakdown Structure and Work Breakdown Structure.



ACTIVITY

1.1.1 Extended Storage Feasibility - a system study to evaluate the technoeconomic feasibility of thermochemical storage concepts in solar energy systems.

1.1.2 Extended Storage Feasibility - an activity complementary to activity 1.1.1.

1.1.3 TES Concept Development - if a need for alternate ideas and concepts for use in solar applications is identified, this activity will seek to fill the need.

1.1.4 Ammonium Hydrogen Sulfate Decomposition - to develop an energy storage concept based upon the decomposition of ammonium hydrogen sulfate.

1.1.5 $Ca(OH)_2/CaO$ Reaction - to develop an energy storage concept based upon the hydration and dehydration of CaO and $Ca(OH)_2$ respectively.

1.1.6 High Temperature Storage and Heat Pipe Analysis - system studies to formulate and evaluate operational chemical cycles.

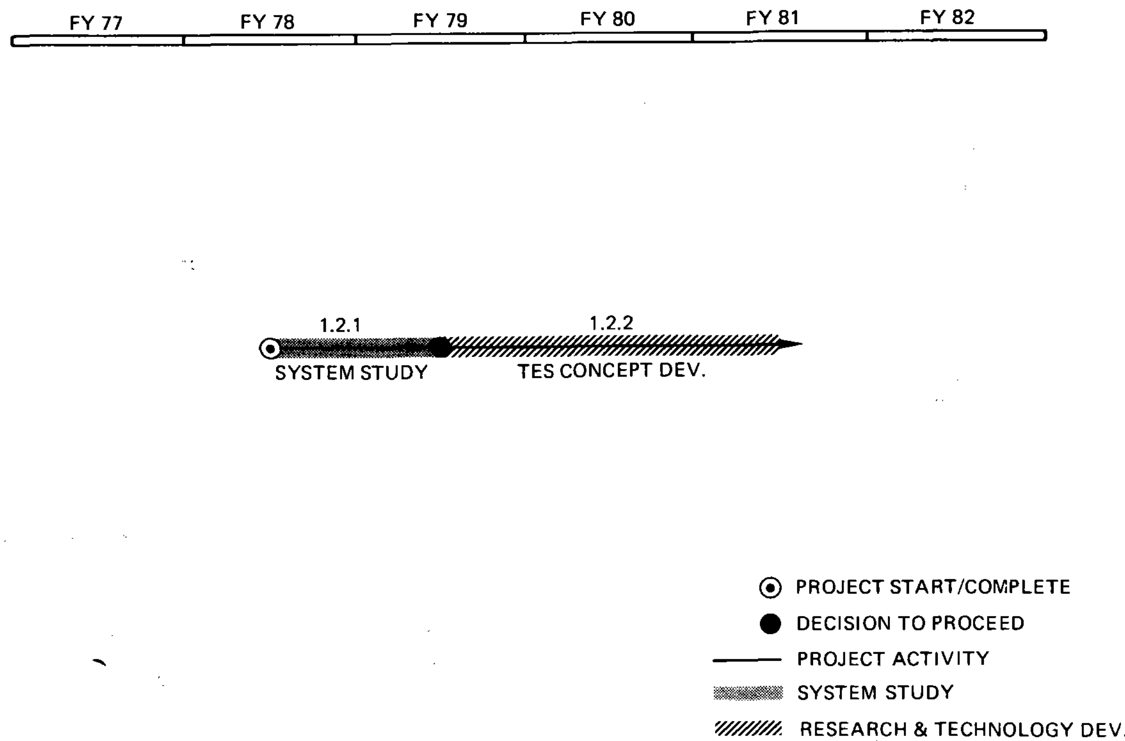
1.1.7 SO_2/SO_3 Concept Development - to develop an energy storage concept based upon the reaction $2SO_3 = 2SO_2 + O_2$.

1.1.8 TES System Development - the continued development of a thermal energy storage concept(s) to the prototype demonstration phase.

4.3 SO_3/SO_2 Catalyst Development - the applicability of current catalysts for use in SO_2/SO_3 storage systems will be determined, and new catalysts developed if required.

4.5 Materials Selection for SO_2/SO_3 TES Systems - assess the availability of metallic alloys and coatings for high temperature containment of SO_2/SO_3 mixture.

Figure 5. TES for Long Duration Solar

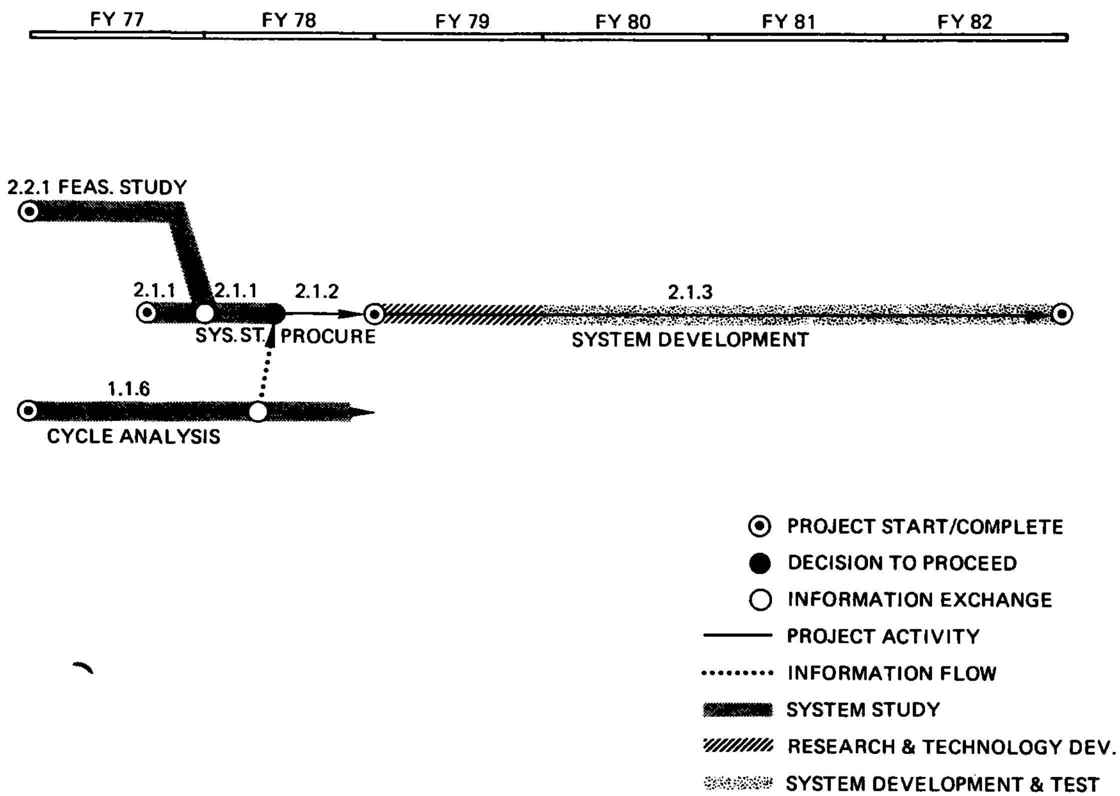


ACTIVITY

1.2.1 TES for Non-Solar Electric Utilities - a system study to evaluate the technoeconomic potential of thermochemical storage concepts in current and near term electric utilities.

1.2.2 TES Development - concept development activities for promising applications identified in 1.2.1.

Figure 6. TES for Non-Solar Utilities



ACTIVITY

2.1.1 Open Heat Pipe Feasibility - a system study to determine the technoeconomic feasibility of the open loop methane based heat pipe.

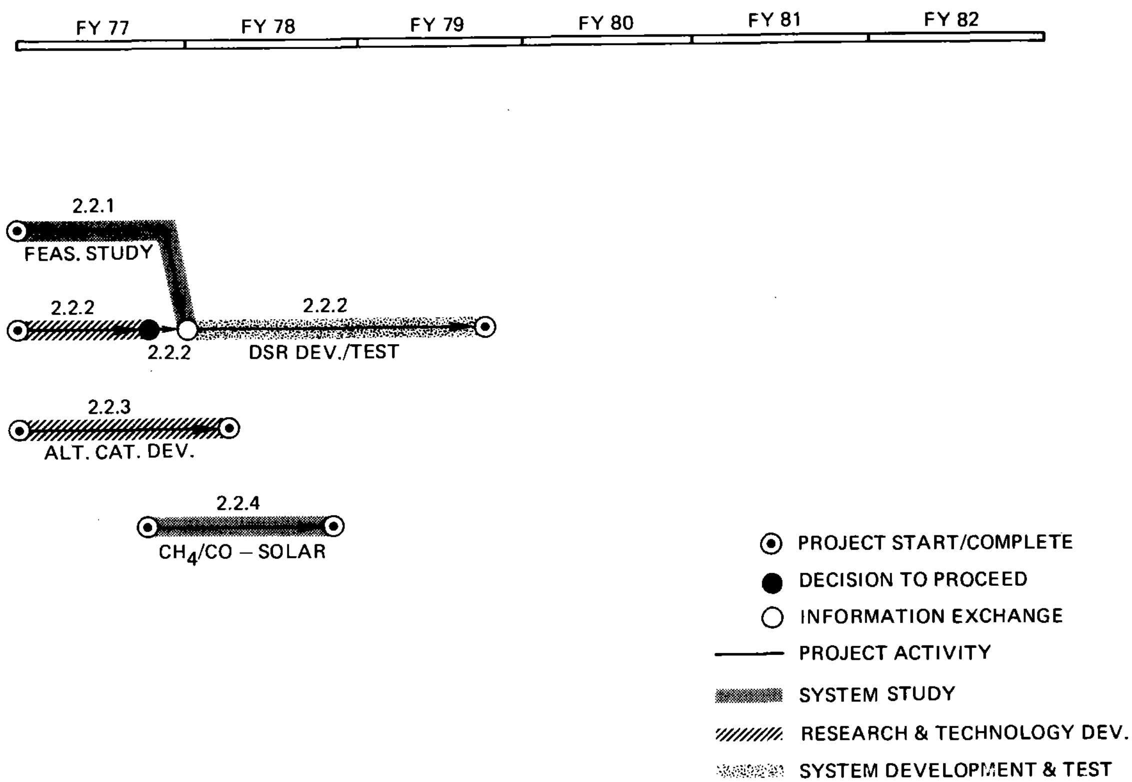
2.1.2 Program Planning - the competitive solicitation and procurement of an activity to develop the open loop methane based heat pipe (see 2.1.3).

2.1.3 Open Pipe Development - the development of an open loop methane based heat pipe.

2.2.1 Heat Pipe Feasibility - a systems study to determine the technical and economic feasibility of chemical heat pipes.

1.1.6 High Temperature Storage and Heat Pipe Analysis - system studies to formulate and evaluate operational chemical cycles.

Figure 7. Open Loop Heat Pipe



ACTIVITY

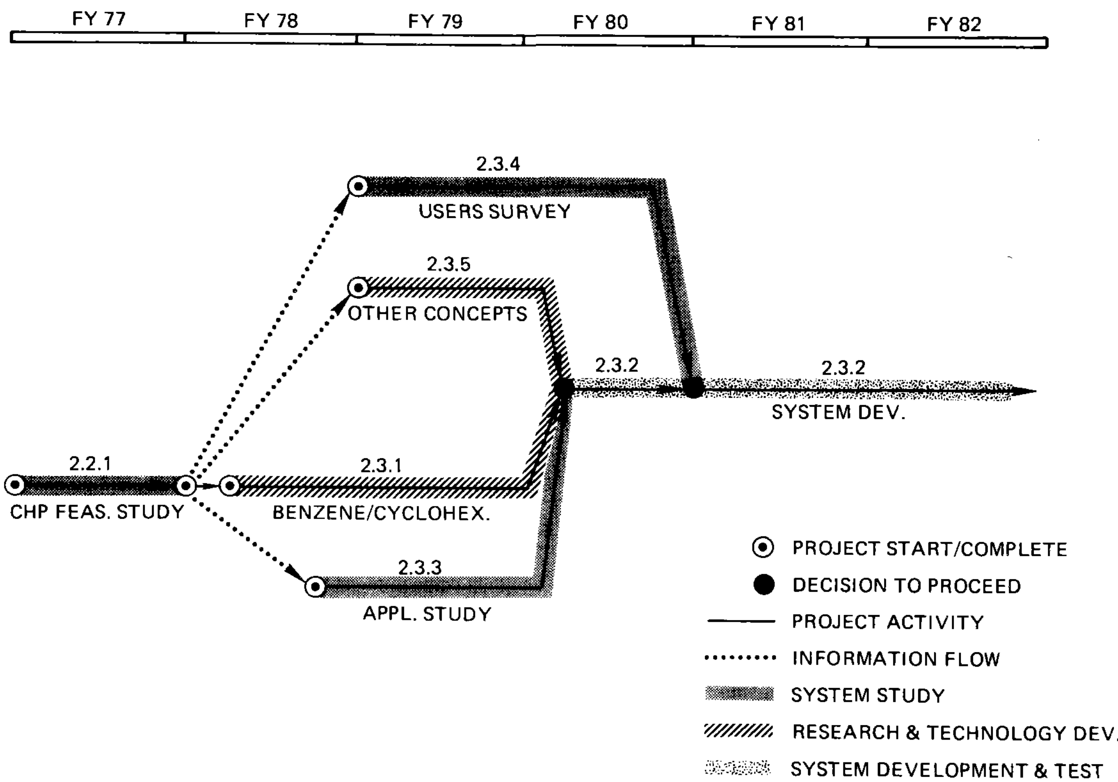
2.2.1 Heat Pipe Feasibility - a systems study to determine the technical and economic feasibility of chemical heat pipes.

2.2.2 Duplex Steam Reformer - to test and evaluate the duplex steam reformer concept at the very high temperature reactor at the Kernforschungsanlage facility in Germany.

2.2.3 Alternate Catalyst Development - to develop alternate catalyst designs used in methanation/reformation reactions.

2.2.4 CH_4/CO Heat Pipe-Solar - a system study to assess the potential of using solar central receivers as the thermal energy source for a methane based heat pipe.

Figure 8. High Temperature Heat Pipe



ACTIVITY

2.2.1 Heat Pipe Feasibility - a systems study to determine the technical and economic feasibility of chemical heat pipes.

2.3.1 Benzene/Cyclohexane Reaction - to develop the benzene/cyclohexane reaction for use in chemical heat pipe systems which can be coupled to thermal sources available in the United States.

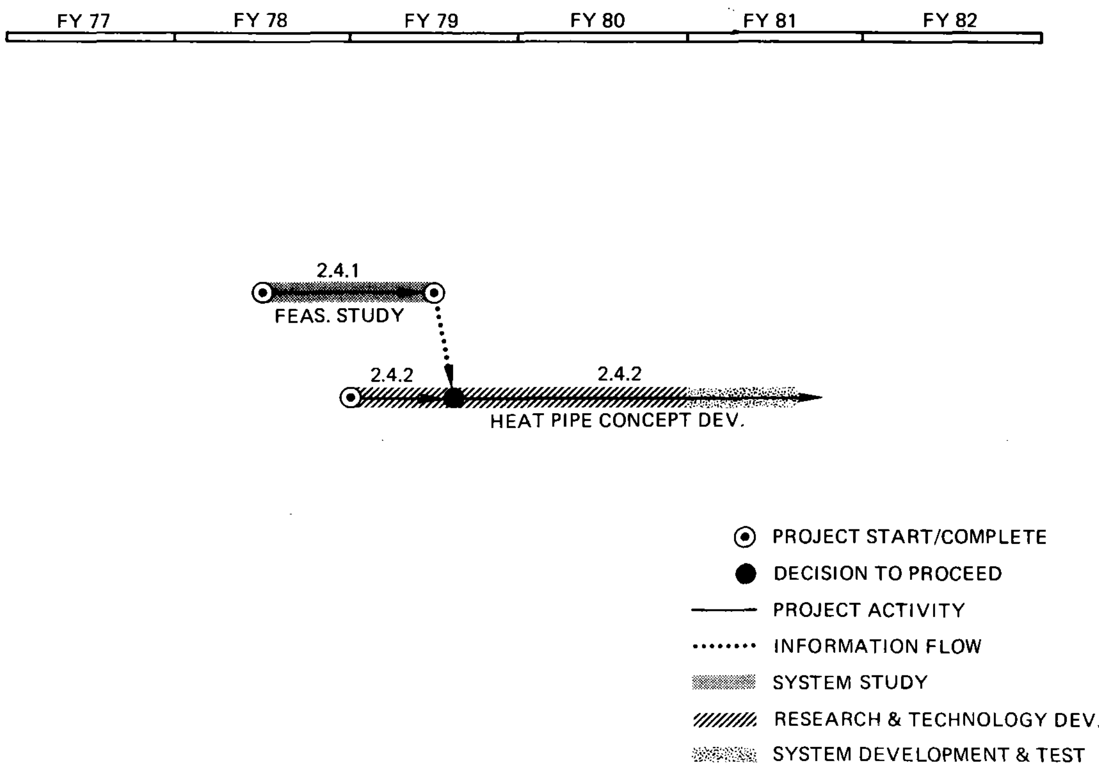
2.3.2 Low Temperature Heat Pipe Development - the continued development of a heat pipe concept(s) to a point of prototype demonstration and test.

2.3.3 Heat Pipe Application Study - system study to critically evaluate and compare alternate means of transporting industrial process heat.

2.3.4 Heat Pipe Users Market Analysis - a study to obtain detailed information concerning potential users of process heat delivered by chemical heat pipes. This information is required for the completion of 2.3.2.

2.3.5 Alternate Heat Pipe Concept Development - to identify and develop concepts other than the benzene/cyclohexane reaction for use in heat pipe systems.

Figure 9. Low Temperature Heat Pipe

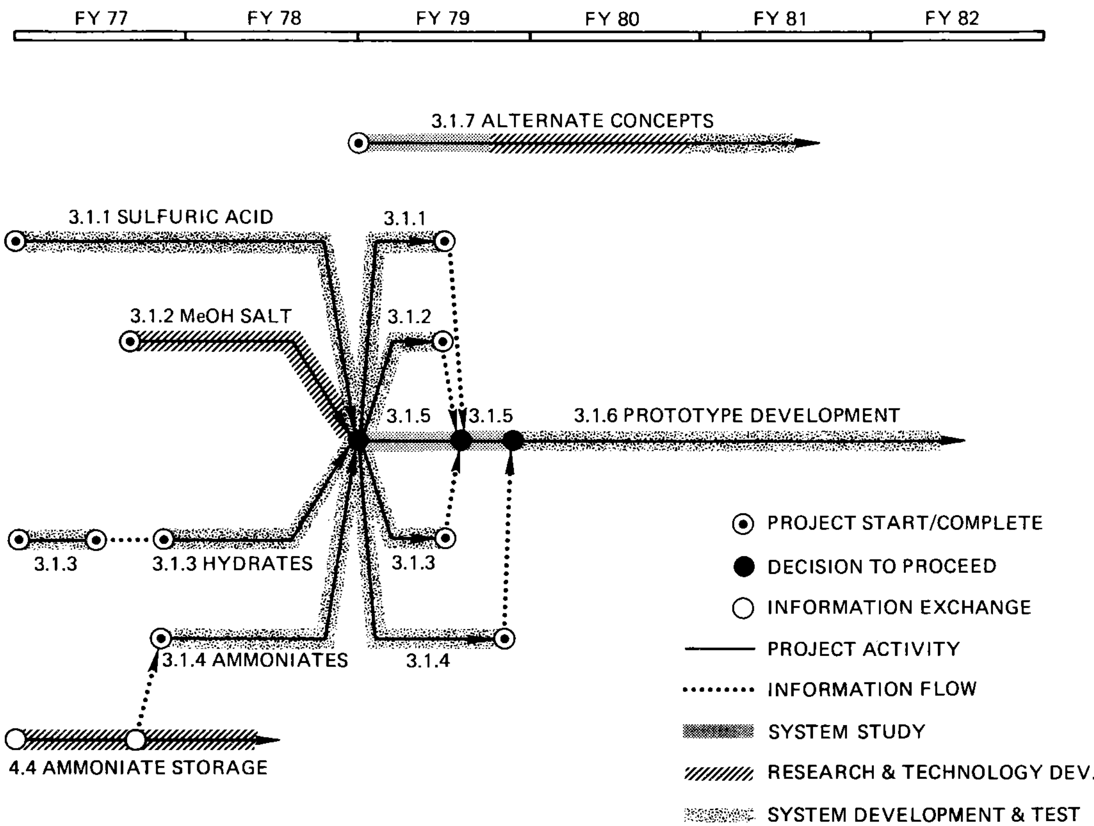


ACTIVITY

2.4.1 Feasibility Study - the use of thermochemical reactions to transport thermal energy in a distributed solar energy will be comparatively evaluated with other approaches.

2.4.2 Heat Pipe Concept Development - assuming a need is identified in 2.4.1, reactions and concepts will be developed for use in distributed solar systems.

Figure 10. Energy Transmission in Distributed Solar



ACTIVITY

<u>3.1.1</u> Sulfuric Acid Concentration/Dilution - a chemical heat pump system based on the concentration/dilution of sulfuric acid will be developed.

<u>3.1.2</u> Methanol-Salt System - a chemical heat pump storage system using methanolated salt reactions will be developed.

<u>3.1.3</u> Hydrated Salt Heat Pump - a chemical heat pump storage system based on hydrated salts, $MgCl_2 \cdot XH_2O$ in particular will be pursued.

<u>3.1.4</u> Ammoniated Salt Heat Pump - to develop a chemical heat pump system based upon the use of coupled ammoniated salt reactions.

3.1.5 Program Planning - the comparative evaluation of all chemical heat pump concepts and the selection of a concept(s) for continued development to the prototype demonstration and test phase.

3.1.6 Prototype Development - the development of a chemical heat pipe concept to prototype demonstration and test.

3.1.7 Alternate Concepts - to identify and develop concepts and reactions for solar heating and cooling in addition to those described in activities 3.1.1, 3.1.2, 3.1.3, and 3.1.4.

<u>4.4</u> Ammoniated Salt Storage - the chemical system characteristics of dissociating ammoniated salts will be determined, (complementary to activity 3.1.4).

Figure 11. Solar Heating/Cooling

TABLE I

FY 77 PROJECTS AND GOALS

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY 77	Status
Thermal Energy Storage Projects				
1.1.1 and 1.1.2	Rocket Research Corp Sandia Labs	Part of a reaction screening study	Select reactions or reaction sequences for solar thermal power plant applications	Complete
			Evaluate selected reactions on basis of thermodynamics and kinetics	In progress
			Perform preliminary design and modeling of reversible chemical reaction storage systems	In progress
			Establish technical and economic feasibility of extended duration storage for solar power plants	In progress
1.1.4	University of Houston	$NH_4HSO_4 + Q \rightarrow NH_3 + H_2O + SO_3$	Conduct literature survey and experimental study to identify reaction sequence for ammonium hydrogen sulfate decomposition	In progress
			Perform kinetic and thermodynamic measurements	In progress
			Design and test flow mode bench scale reactor	In progress
			Evaluate technical and economic feasibility	In progress
			Conduct solar input configuration studies	In progress
Thermal Energy Storage Projects				
1.1.5	Atomics International	$Ca(OH_2) + Q \rightarrow CaO + H_2O$	Determine basic hydration/dehydration properties of $CaO/Ca(OH_2)$	In progress
			Evaluate technical and economic feasibility of fixed-bed, fluidized bed, and rotating drum reactor systems	In progress
1.1.6	Lawrence Berkeley Laboratories	$2SO_3 + Q \rightarrow 2SO_2 + O_2$ $CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Synthesize and evaluate technically feasible flow sheets of storage systems based upon the sulfur trioxide and methane/water chemical systems	Complete

TABLE I (continued)

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY 77	Status
Chemical Heat Pipe Projects				
2.1.1	IGT	$CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Preliminary design of a nuclear (HTGR) and methane-based open-loop system	Complete
			Evaluate energy sources as alternatives to those in the preliminary design (e.g., coal gasification and HTGR/LNG)	Complete
			Assess the feasibility of using existing natural gas pipelines and storage systems for the synthesis gas	Complete
			Assess existing methanation technologies and interchangeability of the SNG with natural gas	Complete
			Evaluate the various alternative energy end-uses for heat, SNG, and electricity	In progress
			Develop two conceptual designs and evaluation of their economics and environmental impacts	In progress
2.2.1	General Electric/ Corporate Research and Development	Primarily $CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Evaluate potential energy sources for chemical heat pipe systems	Complete
			Evaluate alternate chemical systems	Complete
		$C_6H_{12} + Q \rightarrow C_6H_6 + 3H_2$	Establish technical and economic feasibility of methane/steam and benzene/hydrogen systems	Complete
			Assess market for chemical heat pipe	Complete
			Identify critical R&D needs	Complete
2.2.2	General Electric/ Energy Systems Program Dept.	$CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Design, develop fabrication techniques, fabricate, test, and evaluate a duplex steam reformer tube	In progress
2.2.3	General Electric/ Energy Systems Program Dept.	$CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Develop and test an alternate steam reformer catalyst	Program terminated
2.2.4	University of Houston	$CH_4 + H_2O + Q \rightarrow CO + 3H_2$	Optimize process stages and determine process parameters at the steam-reforming-liquid sodium interface of an advanced centered receiver solar thermal power plant	In progress

TABLE I (continued)

Technology Sector	Contractor	Reaction	Major Goals of Projects in Progress in FY 77	Status
Chemical Heat Pump Projects				
3.1.1	Rocket Research Corp.	H_2SO_4 concentration/ dilution	Select concept for detailed sizing and scaling analysis	Complete
			Design and construct a sub-scale closed-loop demonstration system	Complete
			Conduct operational tests to verify system performance	In progress
			Provide recommendations for follow-on work	In progress
3.1.2	EIC Corp.	Salt $(CH_3OH) + Q \rightarrow$ Salt $+ CH_3OH$	Identify combinations of inorganic salt substrates and carrier gases (CH_3OH) suitable for chemical heat pump systems	In progress
			Experimentally determine thermodynamic, kinetic and heat transfer data	In progress
			Perform engineering design and economic analysis	In progress
3.1.3	CES	$MgCl_2 \cdot nH_2O + Q \rightarrow MgCl_2 \cdot mH_2O + (n - m)H_2O$	Perform preliminary design and analysis of chemical treat pump configuration	In progress
			Experimentally investigate rates of water desorption from various salt trydraler	In progress
Generic Research Projects				
4.1	Martin-Marietta/ Colorado State Univ.	Research generic to gas-solid reactions	Determine heat transfer characteristics of a packed bed reactor, in particular, determine effective bed conductivity and solid/gas heat transfer coefficients at imbedded surfaces	Complete
4.2	Univ. of California at Davis	Research generic to gas-solid reactions	Identify and select potential chemical reactions for thermochemical energy storage systems	In progress
			Experimentally investigate reaction kinetics	In progress
4.3	Rocket Research Corporation	$2 SO_3 + Q \rightarrow 2SO_2 + O_2$	Evaluate commercial catalysts and develop a standard activity test	In progress
			If required, develop new catalyst	No activity
			Conduct accelerated aging tests	No activity

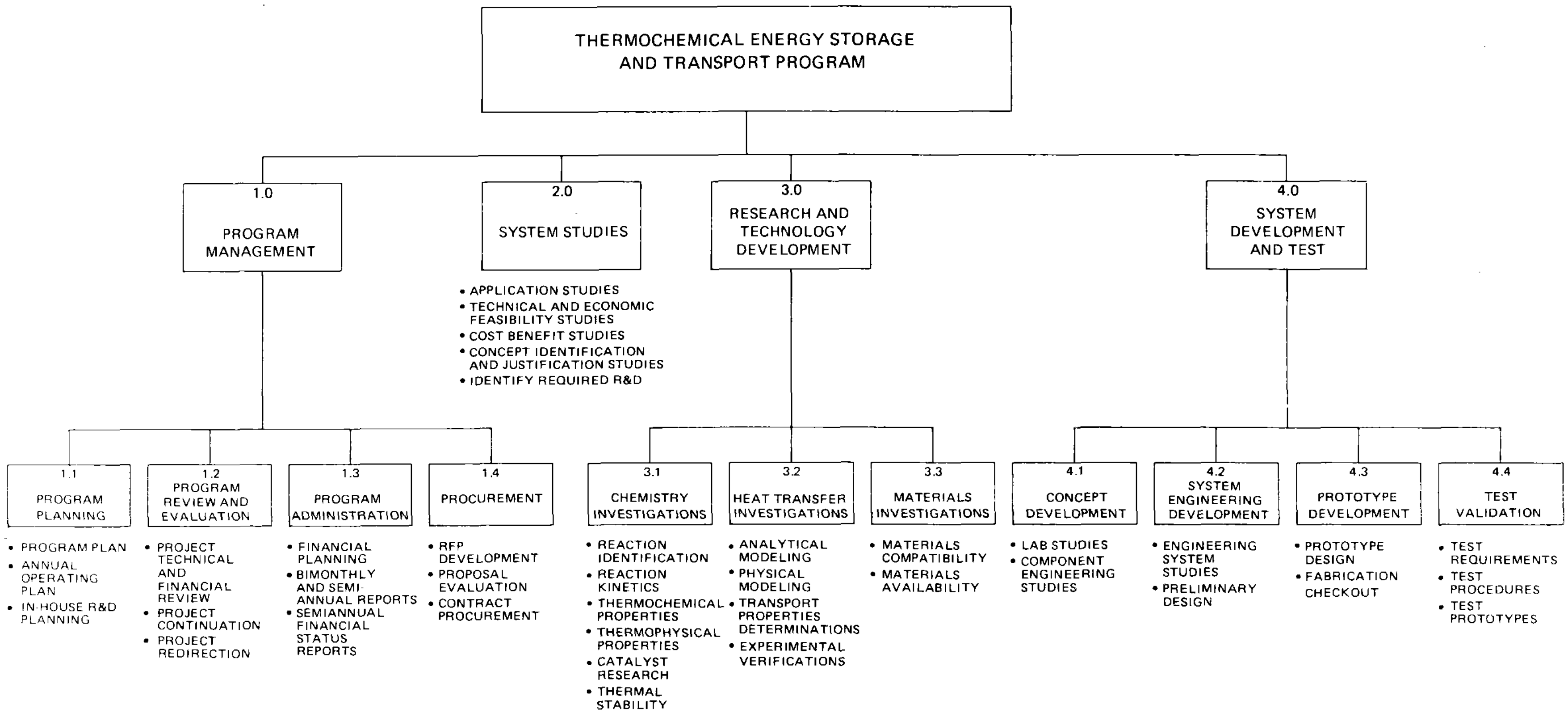


Figure 12. Thermochemical Energy Storage and Transport Program Work Breakdown Structure

Technical Breakdown Structure		Work Breakdown Structure			Project Descriptor (Contractor)
		System Studies	Research and Technology Development	System Development and Test	
Thermal Energy Storage	TES for Long Duration Solar	●			(1.1.1) Extended Storage Feasibility (RRC)
		●			(1.1.2) Extended Storage Feasibility (SLL)
			●		(1.1.4) Ammonium Hydrogen Sulfate Decomposition (UH)
			●		(1.1.5) $Ca(OH)_2/CaO$ Reaction (AI)
		●			(1.1.6) High Temperature Storage/Heat Pipe Analysis (LBL)
Chemical Heat Pipe	Open Loop Heat Pipe	●			(2.1.1) Open Heat Pipe Feasibility (IGT)
	High Temperature Heat Pipe	●			(2.2.1) Closed Heat Pipe Feasibility (GE/CRD)
				●	(2.2.2) Duplex Steam Reformer (GE/ESPD)
			●		(2.2.3) Alternate Catalyst Development (GE/ESPD)
		●			(2.2.4) CH_4/CO Heat Pipe (UH)
Chemical Heat Pump Storage	Solar Heat/Cool			●	(3.1.1) H_2SO_4 Concentration/Dilution (RRC)
			●		(3.1.2) MeOH Salt System (EIC)
				●	(3.1.3) Hydrated Salt System (CES)
Generic Research			●		(4.1) Experimental Heat Transfer (CSU/MM)
			●		(4.2) Thermal Decomposition Kinetics (UCD)
			●		(4.3) SO_3/SO_2 Catalyst Development (RRC)
			●		(4.4) Ammoniated Salt Storage (MM)

Figure 13. Projects Comprising the FY77 Test Program

SUMMARY OF ACCOMPLISHMENTS

Highlights

The following list highlights the major accomplishments for this reporting period. Each project is discussed in more detail under "Program Activities."

1.1.1 and 1.1.2 Rocket Research Corporation and Sandia Laboratories

A compilation was completed of reactions suitable for solar thermal power plants.

1.1.4 University of Houston

Reaction sequences have been identified for ammoniumhydrogensulfate decomposition.

The preliminary design of the flow-mode bench scale reactor has been completed.

1.1.5 Atomics International

Experimental thermal cycling apparatus has been constructed.

1.1.6 Lawrence Berkeley Laboratory

An integrated chemical storage system/power plant has been designed.

2.1.1 Institute of Gas Technology

The preliminary design of an open-loop baseline system has been completed.

Near- and mid-term energy sources for use with open-loop chemical heat pipes have been identified and analyzed.

2.2.1 General Electric/Corporate Research Division

A draft of the final report has been reviewed.

2.2.2 General Electric/Energy Systems Program Department

The final report for the first phase of this program has been received.

Feasibility of explosively forming the duplex steam reformer has been established.

2.2.3 General Electric/Energy Systems Program Department

Alternate catalyst designs have proven impractical to fabricate; consequently the program has been cancelled.

2.2.4 University of Houston

A computer model has been developed to simulate the interface of a high temperature solar system with a methane/steam reformer.

3.1.1 Rocket Research Corporation

A subscale (10^8 Joules), closed-loop, surfulic acid chemical heat pump system has been designed and fabricated.

3.1.2 EIC Corporation

Five promising methanolates have been identified for further investigation.

A comprehensive survey of kinetic studies of salt hydrates has been completed.

3.1.3 CES

Experiments using $MgCl_2$ x H_2O have been conducted to investigate the effects of bed thickness and HCl production.

4.1 Martin-Marietta/Colorado State University

The final report for this project has been received and reviewed.

4.3 Rocket Research Corporation

Commercially available catalyst samples have been obtained; their analysis has begun.

4.4 Martin-Marietta

The final report for this program has been obtained and is under review.

4.5 Sandia Laboratories

An infrared sample cell has been designed for catalyst research.

A literature survey of materials compatible with a SO_2/SO_3 environment has been completed.

Vapor pressure measurements have been performed for magnesium chloride hydrates.

Achievement of TEST Program Goals

The TEST program goals which have been achieved (see Figure 2) are:

Preliminary technical feasibility of the solar chemical heat pump storage concept has been established.

Preliminary technical/economic feasibility of the high-temperature chemical heat pipe has been established.

Preliminary technical/economic feasibility of the low-temperature chemical heat pipe has been established.

Achievement of Project Goals

The FY 77 Project Goals which have been achieved are so indicated in Table I, pages 33 to 36.

PROGRAM ACTIVITIES

In this section, detailed discussions are given of the projects which were ongoing or procurred during the reporting period. Topics discussed include: (1) project objectives and tasks descriptions; (2) technical progress during the past six months; (3) an assessment of contractor performance; and (4) relevant publications. The organization of this section is by Technical Breakdown Structure (TBS). The section concludes with a discussion of program management activities.

Thermal Energy Storage Projects (TBS 1.0)

The following projects are discussed in this subsection:

1.1.1 and 1.1.2	Chemical Energy Storage for Solar Thermal Conversion/Extended Storage Studies
1.1.4	Development of Operational Chemical Cycles for the Storage of Energy
1.1.5	Solar Energy Storage by Reversible Chemical Processes
1.1.6	Chemical Storage of Thermal Energy

PROJECT NUMBER: 1.1.1 and 1.1.2

PROJECT TITLE: Chemical Energy Storage for Solar Thermal Conversion/Extended Storage Studies

CONTRACTOR: Rocket Research Corporation
York Center
Redmond, Washington 98052

Sandia Laboratories
Livermore, California 94550

CONTRACT NUMBER: NSF Grant AER75-22176, ERDA No. 124217 (RRC)

CONTRACT AMOUNT: NSF: $120,000, DOE (ERDA): $150,000 (RRC), $45,000 (SLL)

PREVIOUS CONTRACTS/AMOUNTS: None

PRINCIPAL INVESTIGATORS: R. D. Smith (RRC) and J. J. Iannucci (SLL)

SANDIA TECHNICAL MANAGER: J. J. Iannucci

PROJECT SUMMARY:

Objectives

The overall objective is to evaluate the concept of chemical storage of solar energy on a total system basis. Technical considerations include selection of reactions or reaction sequences which may be useful in reversible-chemical-reaction (RCR) energy storage, evaluation of selected reactions on thermodynamic and kinetic bases, and preliminary design and modeling of energy storage subsystems based on these reactions. A computer model of a solar-thermal, power generation facility (including various RCR energy storage subsystems) is being used to study the technical and economic feasibility of extending the solar-thermal conversion (STC) concept to include baseload power generation.

Tasks

During the two years which have passed since the original proposal was submitted to NSF, certain changes have taken place in the concept of energy storage reversible chemical reactions (RCR) as applied to solar-thermal conversion.

While early concepts were generally tied to a short-term energy storage system (nominally 6 hours), it now appears that long-term storage may offer definite advantages. The scope of the original program has, therefore, been expanded to include a detailed analysis of extending the original concepts to include solar-thermal conversion for baseload power plants. Tasks I, II, and III are the original tasks as proposed for the NSF contract, while Subtasks I through VI represent the work being funded by DOE (ERDA) to extend the original concepts to include baseload applications. These Subtasks have been inserted between Task I and Task II both in practice and in this description.

Task I. Conceptual Development: The objectives of this task are to: (1) select reactions or reaction sequences which may be useful in chemical energy storage systems; (2) tabulate physical, thermochemical, and kinetic properties for these reactions; (3) evaluate the applicable temperature ranges for these reactions; and (4) define a series of baseline cases. A preliminary evaluation of the potential reactions will be performed, and those showing the most promise will be separated into groups suitable for inclusion in the low-temperature (Task II) and high-temperature (Task III studies.

Subtask I. System Selection: Three solar thermal-electric power plant concepts will be selected to integrate with chemical energy storage for a detailed study at baseload capability. The selected concepts will be reduced to mathematical equations describing costs of the components and subassemblies as a function of size and performance.

Subtask II. Baseload System Sizing: Two sites for the location of the baseload solar thermal-electric power plant models will be selected, and by using historical data for each selected site, an average electrical demand load model will be established. Then, by using a storage subsystem with designated round-trip efficiencies, each system will be sized for baseload capacity, and the capital costs of the storage system will be established.

Subtask III. Effect of RCR Energy Storage Subsystems Upon Solar Power Plants and Cost Sensitivity Studies: Guidelines for parasitic powers and heat loss effects will be established. Sandia* will determine: (1) the impact on total electrical output for variable levels of parasitic

*This work performed as part of project 1.1.2.

powers and heat losses, and establish scaling relationships for the STC system, based upon parasitic and storage operational characteristics; (2) identify the unique power plant/storage facilities interfaces and quantify the potential beneficial or detrimental effects; and (3) conduct cost and performance comparisons of the total STC plant using the idealized storage relationships established in Subtask I. The studies will be conducted for grid-connected or grid-independent baseloads and for winter and summer peaking for the locations identified in Subtask II.

Subtask IV. RCR Energy Storage: An integrated, computerized math model will be developed for sizing, performance evaluation, and cost estimation of RCR energy storage systems based on the reactions of interest identified in Task I.

Subtask V. Optimization of Solar Thermal-Electric Power Plants: Each of the three systems selected in Subtask I will be optimized for baseload capability (plus intermediate and peaking, if applicable) with the SO_2/SO_3 storage system. Capital costs and energy costs will be calculated. Parametric studies will be performed on each system to identify the cost sensitivities of various parasitic powers in the major components and subsystems.

Recommendations for pusuing baseload solar power plants will be provided by RRC and Sandia,* and a detailed development plan to attain long-range goals will be established.

Subtask VI. Chemical Energy Storage Plant Specifications: Two sets of power plant requirements will be established for use in the preliminary design effort of the basic NSF/ERDA program. The requirements will be nominally for a high- and low-temperature system.

The specifications will be generalized from the optimum plant sizes established in Subtask V. The specifications that will be fixed include:

Power Level(s)	Operating Temperature(s)
Storage Capacity	Site Location

*This work performed as part of project 1.1.2.

Tasks II and III. Low- and High-Temperature Systems Analysis: Five reaction sequences in each of the temperature range of 400°K to 1300°K will be selected for a detailed engineering study and evaluation.

Technical Progress

Tasks I, II, and III. Reaction Selection and Evaluation: All of Task I and the thermodynamic and kinetic analyses of Tasks II and III are complete. Based on the following criteria, 85 candidate reactions were identified:

1. Reaction appears to be reversible
2. $\Delta H_R \geqq 110$ kcal/kg
3. $|\Delta G_{298°K}|$ or $|\Delta G_{800°K}| \leqq 100$ kcal/mole
4. Approximate equilibrium temperature $T \approx \Delta H/\Delta S$ in the range of 400°K to 1300°K.

Nearly all of the 85 reactions could be classified into 14 categories based on the reaction or chemical type. The final selection of 24 reactions is the result of trying to select the highest rated reactions from each category while also including reactions which were known to be under investigation by other workers. A data book has been assembled which includes, for each of the 24 selected reactions, such information as theoretical energy content, endothermic and exothermic reaction temperature, physical state and density of reactants and products at 298°K, estimated storage round-trip efficiency, and a simplified process flow sheet for a storage subsystem.

Completion of Tasks II and III of the original program will be delayed pending completion of the six subtasks of the supplementary effort.

Subtasks I, II, III, IV, V, and VI - Extended Storage Model

Subtask I. System Selection: Three solar thermal-electric power plant systems have been selected for modeling and extension to baseload capability. They include:

1. Central receiver collection, Rankine cycle power generation (783 K)

2. Central receiver collection, open-brayton cycle power generation (1310 K)

3. Distributed collection, Rankine cycle power generation (588 K)

Each of these systems has been broken down into subsystems, and each subsystem has been modeled with respect to energy efficiency and capital cost as a function of size.

Subtask II. Baseload System Sizing: Four hypothetical location sites have been selected for a STC power plant: Miami, Florida (SE), Milwaukee, Wisconsin (NC), Albuquerque, New Mexico (SW), and New York, New York (NE). Hourly profiles of direct-normal insolation and electrical grid load have been obtained for each location for at least one representative year. Baseload sizings have been calculated for a high-temperature, Brayton cycle STC system for 100 MWe baseload service (see Subtask IV below).

Subtask III. Effect of RCR Energy Storage Subsystems Upon Solar Power Plants and Cost Sensitivity Studies: Sandia has used its central STC plant cost/performance expertise to aid Rocket Research in system selection, baseload sizing, and general modeling concepts required by this study. Rocket Research has shared valuable chemical process analysis and detailed load information with Sandia to aid Sandia's efforts to analyze the worth of long-term storage in "stand alone" plants. Subtask III information exchanges will continue until the completion of the other RRC subtasks. Future Subtask III work may center on system optimization.

Subtask IV. RCR Energy Storage: A system-sizing computer program has been written as a first step toward the overall computer model. This program uses the subsystem models and insolation/demand data described above, and by means of an iterative hour-by-hour energy balance over the course of a year, computes the required size of each subsystem for a specified load profile (baseload, baseload plus intermediate, or grid independent) and storage round-trip efficiency, η_{RT}.

Some preliminary results of the sizing of a high-temperature, Brayton cycle STC system for 100-MWe baseload service have been obtained. The most surprising results of this preliminary analysis are the near identical collector areas required at locations NC and SE for all values of η_{RT}. Since collectors account for as much as half the total plant cost in most current designs, it appears that inclusion of extended storage capability may lessen considerably the effects of latitude and extended bad weather on the feasibility of baseload solar-thermal power generation. It should be emphasized that these results are preliminary, however, and further conclusions must await development of the complete cost and performance model. This part of Subtask IV has been merged with Subtask II since the code development and utilization are intimately connected.

Subtasks V and VI. Optimization of Solar Thermal-Electric Power Plants and Chemical Energy Storage Plant Specifications: A small amount of work has been completed on these subtasks in advance of expected start dates. The complexity of these subtasks has suggested that some advance work of a preliminary nature was justified.

Technical Problems

No apparent technical problems will be encountered in the completion of this work. Should additional detailed analysis that is clearly beyond the scope of the original contracts be required of RRC, there could be schedule and/or cost impacts. An area of concern in this regard is the Subtask V work on power plant optimization. Depending on the level of sophistication of the optimization required, the number of system and plant locations involved, and the number of chemical reactions involved (other than SO_2/SO_3), some trade off may occur between computer charges and schedule slippages. Subtask V is specific to SO_2/SO_3 but RRC feels the spirit of the study intended for several chemical systems to be optimized. Sandia concurs and will support such a broadening of the statement of Subtask V to include other candidate reactions. At present, RRC hopes such a broadening can be completed with no schedule or cost impact.

Program Management

The Sandia technical manager has had the highest level of cooperation and assistance from Rocket Research during the past six months. They have performed all tasks promptly, thoroughly, and within budget.

Publications

1. Huxtable, D. D. and Schmidt, G., "Chemical Energy Storage for Solar Thermal Conversion," Interim Report No. 2, 77-R-558, Rocket Research Corp., Redmond, Washington, April 1977.

2. Huxtable, D. D. and Schmidt, G., "Chemical Energy Storage for Solar Thermal Conversion," Quarterly Report No. 1, 76-R-538, Rocket Research Corp., Redmond, Washington, October 1976.

PROJECT NUMBER: 1.1.4

PROJECT TITLE: Development of Operational Chemical Cycles for the Storage of Energy

CONTRACTOR: University of Houston
Houston, Texas 77004

CONTRACT NUMBER: EG-77-C-04-3974

CONTRACT PERIOD: May 1977 to May 1978

CONTRACT AMOUNT: $250,000

PREVIOUS CONTRACTS/AMOUNTS:

PRINCIPAL INVESTIGATORS: W. E. Wentworth, W. W. Prengle, A. F. Hildebrandt

SANDIA TECHNICAL MANAGER: Reginald E. Mitchell

PROJECT SUMMARY:

Objectives

The overall objective of this program is to find, develop, and demonstrate a chemical reaction cycle which can be used for solar storage and regeneration in electrical power generation systems which operate within the temperature range of 450-500 C. In particular, the thermal decomposition of ammonium hydrogen sulfate (NH_4HSO_4) into ammonia (NH_3), water (H_2O), and sulfur trioxide (SO_3) is being investigated for the energy storage step

$$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3$$

and the reverse recombination reaction for the energy regeneration step

$$NH_3 + H_2O + SO_3 \rightarrow NH_4HSO_4$$

Tasks

The program includes the efforts of three research groups (identified as Phases 1A, 1B and 1C) which work separately but coordinate their efforts and planning through bi-weekly meetings. The first phase is a laboratory investigation which addresses fundamental chemistry problems; the second phase is concerned with the chemical engineering aspects of the system; and the third phase is concerned with characterizing the solar energy input conditions.

Phase 1A. Chemical Reaction Fundamentals: Various reaction mechanisms will be screened (by means of literature surveys and experiments) in search of net reaction cycles which are equivalent to the energy storage and regeneration reactions and which allow satisfactory separation of SO_3 from NH_3 and H_2O at high temperature. After suitable reaction mechanisms (including separation procedures) are identified, appropriate kinetic and thermodynamic measurements will be made on the decomposition and recombination steps of each. These will be used to establish the best reaction conditions for each mechanism. A high-pressure reactor will then be designed to study the individual mechanisms under operational conditions and to test their long-term reversibility.

Phase 1B. Process and Engineering Configuration: The most suitable chemical reaction cycle selected through the work of Phase 1A will be investigated in a flow mode. Design equations will be developed and used to design a flow mode bench-scale reaction unit. The flow reaction kinetics and heat transfer characteristics will be studied for each reaction step in the cycle. These results will then be used to design and specify a pilot unit. The economics and technical feasibility will be under constant consideration.

Phase 1C. Solar Energy Input Configuration: Solar input configuration studies will be conducted simultaneously with the work of Phases 1A and 1B. These will involve location and evaluation of parabolic solar concentration systems, establishment of specifications, procurement of a suitable concentrator, and preliminary heat transfer studies. Materials suitable for a solar-heated reactor will be identified. A conceptual design will be developed for a full-scale demonstration plant including storage. The basic cost estimates will also be developed for the chemical storage portion of a solar tower electrical system.

PROJECT STATUS:

Technical Progress

Phase 1A. Chemical Reaction Fundamentals: The following mechanism has been found to be promising as a way of accomplishing energy storage with separation of products:

$$NH_4HSO_{4(sol)} + M_2SO_{4(sol)} \rightarrow NH_{3(g)} + H_2O_{(g)}$$

$$M_2S_2O_{7(sol)}$$

$$M_2S_2O_{7(sol)} \rightarrow M_2SO_{4(s)} + SO_{3(g)}$$

where M is any group 1A metal. Equilibrium pressure measurements from 100 to 1050°C from mixtures of NH_4HSO_4 and the Group 1A sulfates show that the best separation of SO_3 from NH_3 and H_2O occurs with Cs_2SO_4;

$$Cs_2SO_4 > Rb_2SO_4 > K_2SO_4 > Na_2SO_4 > Li_2SO_4$$

Experimentation has shown that the yield of NH_3 obtainable at a given temperature is strongly dependent not only on the metal sulfate employed, but also on the heating rate.

The decomposition of NH_4HSO_4 in the presence of metal oxides is also under investigation. This two-step scheme is given by

$$NH_4HSO_{4(s)} + MO_{(s)} \rightarrow NH_{3(g)} + HO_{(g)} + MSO_{4(s)}$$

$$MSO_{4(s)} \rightarrow MO_{(s)} + SO_{3(g)}$$

where M is a metal. When zinc is employed as the metal, the separation is good; however, the $ZnSO_4$ formed does not decompose under 870°C. At this high temperature, SO_3 also decomposes, which is a serious disadvantage. Other metal oxides are under consideration.

Phase 1B. Process and Engineering Configuration: Transport and thermodynamic data have been obtained from the literature, and work has begun on tabulating and correlating properties of reactants and products as a function of temperature.

A preliminary bench-scale design has been completed in which the decomposition of NH_4HSO_4 in the presence of metal sulfates can be investigated in a flow mode.

Phase 1C. Solar Energy Input Configuration: Equations have been set up for calculation of focal plane flux profiles for both a simple parabolic reflector and a Cassegrainian reflector system.

Technical Problems

The failure of two chemical supply companies to deliver ordered amounts of NH_4HSO_4, the basic chemical in the proposed reaction cycle, is causing a serious delay in the fulfillment of several tasks in Phase 1A. The current supply of this chemical has been exhausted. Delivery was expected from a third company in mid-September.

Due to budgetary and procedural negotiations, the money for this program was not available for expenditure until two months after the official starting date. This resulted in a two-month delay in placing equipment orders, and hence delays in tasks involving product analysis in Phase 1A.

Program Management

The technical achievements have been exceptional. Despite the budgetary delays, most project schedule objectives are being met and some objectives are even ahead of schedule. Cost objectives are also being maintained.

Publications

1. W. E. Wentworth, C. F. Batten, G. E. Corbett and E. C. M. Chen, "An Ionic Model for the Systematic Selection of Chemical Decomposition Reactions for Energy Storage," in Proceedings of the 1977 Annual Meeting, published by American Section of the International Solar Energy Society, 300 State Road 401, Cape Canaveral, Florida 32920, p. 18-1, 1977.

2. W. E. Wentworth, A. F. Hildebrandt, C. F. Batten, G. E. Corbett and E. C. M. Chen, "Thermal Chemical Conversion Cycles for Storage of Solar Energy," submitted to Review Internationale des Hautes Temperatures et des Refractaires.

3. W. E. Wentworth, C. F. Batten and E. C. M. Chen, "Thermochemical Conversion and Storage of Solar Energy," submitted to Proceedings of the International Symposium on Energy Sources and Development.

4. C. E. Mauk, H. W. Prengle, Jr., and E. Sun, "Off-Axis Concentration in a Cassegrainian Solar Collector," to be published.

Presentations

1. W. E. Wentworth, C. F. Batten, G. E. Corbett and E. C. M. Chen, "An Ionic Model for the Systematic Selection of Chemical Decomposition Reactions for Energy Storage," 1977 Annual Meeting of the American Section of the International Solar Energy Society held in Orlando, Florida, June 6-10, 1977.

2. W. E. Wentworth, A. F. Hildebrandt, C. F. Batten, G. E. Corbett and E. C. M. Chen, "Thermal Chemical Conversion Cycles for Storage of Solar Energy," International Colloquim held in Odeillo/ Fontromeu, France, June 28-30, 1977.

3. C. E. Mauk, H. W. Prengle, Jr., and E. Sun, "Off-Axis Concentration in a Cassegrainian Solar Collector," Joint Conference of the Texas, New Mexico and Arizona Solar Energy Societies held in Dallas, Texas, August 27-28, 1977

PROJECT NUMBER: 1.1.5

PROJECT TITLE: Solar Energy Storage by Reversible Chemical Processes

CONTRACTOR: Atomics Internationational
8900 De Soto Ave.
Canoga Park, California 91304

CONTRACT NUMBER: EY-76-C-03-0701, Task 33

CONTRACT PERIOD: August 8, 1977 - January 23, 1978

CONTRACT AMOUNT: $90,800

PREVIOUS CONTRACTS/AMOUNT: AER 74-09069-A01/$

PRINCIPAL INVESTIGATOR: G. Bauerlee

SANDIA TECHNICAL MANAGER: M. Nichols

PROJECT SUMMARY:

Objective

The overall objective is to verify the technical feasibility and economic attractiveness of the $CaO/Ca(OH)_2$ reversible chemical solar energy storage concept.

Tasks

In order to meet the above objective, the current phase of the program consists of the following tasks:

Task 2. Basic Hydration/Dehydration Properties of $CaO/Ca(OH)_2$: The objective of this work is to: (1) verify that a fixed-bed configuration of calcium oxide/hydroxide can be chemically cycled over a large number of cycles without degrading in terms of bed utilization, and (2) ascertain the inherent energy content in and intrinsic chemical reaction rate of CaO relative to the solar cycle.

Task 3. Fluidized Bed System Analysis: The objective is to analytically evaluate the technical and economic viability of the fluidized bed system for extracting energy from and putting energy into the metal oxide/hydroxide. The system requirements will be established, a conceptual design will be developed, the system performance will be established, the design uncertainties will be identified, an economic assessment will be made, and plans for experiments will be prepared.

Task 4. Rotating Drum Reactor System: The objective is identical to that of Task 3 except that a rotating drum system is to be studied.

Task 5. Evaluation, Assessment, and Ranking of Three Systems: The objective is to derive an initial ranking of the three storage concepts (fixed-bed, fluidized-bed, and rotating drum) in terms of near-term technical and economic viability.

PROJECT STATUS:

Technical Progress

Task 2. Characterization of as-received, reagent-grade $Ca(OH)_2$ has continued. Results obtained to date include analyses of metals, surface area measurements, crystal habit and size distribution, and chemically bound water. Remaining analyses required to complete the initial characterization include an independent analysis for hydrate water and for noncondensible adsorbed gases.

Tasks 3 and 4. Work was accomplished in three areas: (1) data collection, (2) data workup, and (3) system design. Thermal properties of CaO, $Ca(OH)_2$, and H_2O were obtained from JANAF data and used to compute and plot the heat of reaction and equilibrium dissociation pressure for the hydration/dehydration reaction,

$$CaO(C) + H_2O(g) \rightleftarrows Ca(OH)_2$$

over a range of temperature from 298 to 877 K. Several National Lime Association data books were obtained which describe lime properties and the handling and storage methods. Recent survey articles, symposium papers, and texts on fluidized beds, pneumatic conveying, and rotating drum drying have also been obtained.

The baseline design parameters selected for the proposed design are listed below:

Day Operation Maximum Net Power - 100 MWe

Night Operation Maximum Net Power - 100 MWe

Maximum Energy Storage - 420 MWhe Net

Maximum Solar Power - 506 MWt @ noon, summer solstice

Solar Multiple - 1.89

Maximum Charging Rate to Storage - 217 MWt (depending on parasitic losses)

Task 5. No progress was made during this period.

Technical Problems

Interpretation of the preliminary results obtained with the DSC 1B at the Science Center has been difficult. The measured ΔH appears to be low and does not correlate with the percent dehydration. However, since these are exploratory runs, the situation is not serious. Several improvements in the procedures to be used with the PDSC, have been suggested by this work.

Program Management

Only one month of work has been completed during this reporting period so it is still too early for an objective assessment. At this point, the schedule is being met.

A realistic gauge of the future success of CaO - $Ca(OH)_2$ system will be the success or failure of the cycling tests that are just being started.

PROJECT NUMBER: 1.1.6

PROJECT TITLE: Chemical Storage of Thermal Energy

CONTRACTOR: Lawrence Berkeley Laboratory
and the Department of Chemical Engineering
University of California
Berkeley, California 94720

CONTRACT NUMBER: W-7405-ENG-48

CONTRACT PERIOD: October 1976 to September 1977

CONTRACT AMOUNT: $88,000

PREVIOUS CONTRACTS/AMOUNT:

PRINCIPAL INVESTIGATORS: Scott Lynn, Alan Foss

SANDIA TECHNICAL MANAGER: Carl C. Hiller

PROJECT SUMMARY:

Objectives

Program objectives are to design and analyze technically feasible, high-temperature, reversible chemical reaction energy storage systems for solar thermal power plants. Moreover, baseline equipment requirements, system efficiencies, and capital costs are to be estimated, and common methods for comparing alternative energy storage concepts are to be outlined.

Tasks

Specific project tasks are

1. Develop a flowsheet for the baseline SO_2/SO_3 system which optimizes thermal efficiency by integrating the simultaneous operation of the storage and power plant systems.

2. Develop a similar flowsheet for the CH_4/H_2O system and compare the relative advantages of the two systems.

3. Identify and study specific problems and limitations associated with the SO_2/SO_3 energy storage system.

4. Identify a potential method of comparing sensible and chemical heat storage approaches on an equivalent basis, and perform a limited preliminary cost-performance analysis.

5. Review and analyze research reports submitted by other DOE contractors.

PROJECT STATUS

Technical Progress

Tasks 1, 2, and 3 have been successfully carried through a first iteration, and the work has brought about a much greater understanding of chemical storage systems. One potential chemical energy storage/power plant integration scheme applicable to the SO_2/SO_3 concept was studied in detail. This study has laid the groundwork for future comparisons of alternative storage/plant design and integration concepts for many types of chemical energy storage. Specific problems associated with both technical limitations and relative storage/plant sizings have been identified, and alternative configurations are currently under study.

A potential, although limited, method for comparing high-temperature sensible and chemical storage systems has been proposed, and a limited cost-performance comparison of magnesia brick sensible storage versus SO_2/SO_3 chemical storage is currently under way. Meetings are scheduled with NASA Lewis early in November to coordinate the latter effort and to attempt to mutually arrive at a more flexible method of comparison.

LBL has also been asked to review numerous reports and proposals submitted by other contractors; their concise criticisms have proved invaluable in identifying both technical and cost analysis shortcomings.

Technical Problems

No significant technical problems which could have an effect on program schedule or budget have been encountered.

Program Management

Management of the program has been satisfactory. The probable increasing importance of the LBL analyses in the chemical energy storage program is expected to bring about a closer coordination of efforts between LBL and Sandia.

Publications

1. J. Dayan, S. Lynn, A. Foss, "Evaluation of a Chemical Heat Storage System for a Solar Steam Power Plant," Procedures of the 12th Intersociety Energy Conversion Engineering Conference (published by the American Nuclear Society, 1977).

Chemical Heat Pipe Projects (TBS 2.0)

The following projects are discussed in this subsection:

2.1.1 Transmission of Energy by Open Loop Chemical Energy Pipelines

2.2.1 Closed Loop Chemical Systems for Energy Storage and Transmission

2.2.2 Duplex Steam Reformer Development Program

2.2.3 Alternate Catalyst Development Program

2.2.4 Cyclic Catalytic Solar Energy Storage Systems

PROJECT NUMBER: 2.1.1

PROJECT TITLE: Transmission of Energy by Open Loop Chemical Energy Pipelines

CONTRACTOR: Institute of Gas Technology
3424 South State Street
IIT Center
Chicago, Illinois 60616

CONTRACT NUMBER: 87-9181

CONTRACT PERIOD: May 1977 to January 1978

CONTRACT AMOUNT: $100 K

PREVIOUS CONTRACTS/AMOUNT:

PROJECT MANAGER: Thomas P. Whaley

PROJECT SUPERVISOR: Nathaniel R. Baker

SANDIA TECHNICAL MANAGER: Reginald E. Mitchell

PROJECT SUMMARY:

Objectives

The project will assess the technical-economic feasibility of two specific near-term and mid-term cases of energy transport via open-loop, methane-based, reversible chemical reactions.

Tasks

Task 1. Preliminary Design: The objective of this task is to develop a preliminary design for an open-loop system. This work consists of: (a) the synthesis and technical-economic evaluation of an open-loop, reversible chemical reaction energy transport and storage system; (b) the preliminary identification of institutional and safety problems associated with the system; and (c) the selection of two specific cases (a near-term and a mid-term) for more detailed analysis during the remainder of the program.

Task 2. Alternative Energy Sources: This task is aimed at identifying energy sources, other than nuclear, capable of driving the methane reforming reactions.

Task 3. Synthesis Gas Storage and Pipelines: The cost of transmitting and storing CO/H_2 mixtures in the existing natural gas pipeline system will be assessed. The alternative of modifying or replacing the natural gas compressors and of adding additional pipelines will be evaluated.

Task 4. Methanation Technology and SNG Interchangeability: In this task, various methanation process schemes will be reviewed and that scheme which has the most advantage with regard to thermal duties and SNG quality will be optimized and evaluated economically.

Task 5. Alternative Energy Uses: Utilization scenarios for SNG and heat (the end-products of the chemical energy pipeline) will be developed. Bounds will be identified for determining under what conditions the product heat should be used for electrical generation. Other uses of the heat, such as process steam, district heating, etc., will be evaluated for feasibility and economics.

Task 6. Technical-Economic Evaluation and Conceptual Design: The economics and environmental impact of the CHP systems synthesized in the above tasks will be assessed. Areas which may require further development before an operating system could be built will be identified.

PROJECT STATUS

Technical Progress

Task 1. Preliminary Design. An open-loop base case design consisting of a 3000-MW_t HTGR, a steam reformer, 100 miles of pipeline, and a methanation plant has been synthesized. The output from the methanation plant is 1531 MW_t of process steam and 2.2×10^7 nm^3/day of SNG (heating value 33.3 MJ/m^3). The calculated cost based on utility financing for this energy is 20.4 mills/kWhr for the process steam, with SNG being assigned a value equal to an equivalent amount of methane on a heating-value basis.

It has been determined that the SNG output from the methanation plant can be blended with three typical domestic natural gases as follows:

Natural Gas Type	Allowable Concentration of SNG, %(V/V)
High Methane	70
High Inert	100
High Heating Value	65

Methanol and acetone have been identified as undesirable by-products (trace amounts) formed in the methanator.

Task 2. Alternative Energy Sources. The following near-term application has been identified; a coal gasification plant consisting of a U-gas gasifier and a shift reactor to obtain the correct H_2/CO ratio. Its output is approximately equal to that of the 3000-MW_t nuclear base case design.

The following mid-term application has been identified: an ocean-based HTR (3000 MW_t) combined with an LNG terminal, desalination unit, and steam reforming plant. The design is based on a scaled-up version of the General Electric 500-MW_t, pebble-bed, gas-cooled reactor. The output from the plant complex (located within three miles of shore) is transmitted to shore via an undersea pipeline.

Task 3. Synthesis Gas Storage and Pipelines. A review of underground storage techniques has shown that it should be possible to store synthesis gas in either an underground aquifer, salt strata, or depleted gas wells that are properly sealed.

Existing natural gas transmission systems that have the inherent capacity to carry the 6.37×10^7 m^3/day of reformed gas have been located. These pipeline systems carry gas from the Texas, Oklahoma and Louisiana region to Minnesota, Illinois, Indiana, Pennsylvania and New York.

Task 4. Methanation Technology and SNG Interchangeability. A review of methanation processes did not produce any one design that was clearly superior to the others. IGT's own methanation process has been chosen for the design of the methanation complex primarily because detailed cost and design information is already available. Energy and material balances, heat availability estimates, and methanation reactor design have been completed.

Technical Problems

No technical problems have been identified to date which have had or could have a significant impact on the technical, schedule, or cost objectives of the program.

Program Management

The technical performance of IGT during this reporting period has been outstanding. The program has proceeded according to schedule, and a level of effort (both in manpower and money) in line with projections has been maintained.

Publications

1. N. Baker, et al., "Transmission of Energy by Open-Loop Chemical Energy Pipelines, Project 8990, First Quarterly Progress Report, Institute of Gas Technology, Chicago, Ill., September 1977.

PROJECT NUMBER: 2.2.1

PROJECT TITLE: Closed Loop Chemical Systems for Energy Storage and Transmission

CONTRACTOR: General Electric Company
Corporate Research Division
P. O. Box 8, Bldg. K-1
Schenectady, NY 12305

CONTRACT NUMBER: EY-76-C-02-2676*000

CONTRACT PERIOD: June 15, 1975 - September 30, 1977

CONTRACT AMOUNT: $303,300 (215,300 Basis, $88,000 MOD I)

PREVIOUS CONTRACTS/AMOUNT:

PROGRAM MANAGER: James B. Comly

PRINCIPLE INVESTIGATORS: Himanshu B. Vakil, John Flock

SANDIA TECHNICAL MANAGER: James J. Bartel

PROJECT SUMMARY:

Objectives

The objectives of this program are to assess the technical and economic feasibility of high and low temperatures energy transport systems based upon the use of reversible chemical reactions, and to identify required research and development.

Tasks

Task 1. Process Design Development: A preliminary process design is to be developed for each of the closed-loop chemical systems for energy storage and transport. The major goal is the development of computer codes to study the effect of various design choices on heat exchanger sizes, volume of gases to be pumped (or stored), storage density, compressor/expander duties, and overall first law efficiency. In addition to total heating and cooling duty, temperature levels at which heat is supplied (or withdrawn) are obtained.

Task 2. Assessment of Chemical Reactions: Various alternatives to the Adam/Eva or CH_4/CO_2 (HYCO) reactions shall be examined. Variations of the CO/H_2 ratios between one (HYCO) and three (Adam/Eva) shall also be examined. A search shall be conducted for suitable reactions that can be coupled to intermediate temperature primary sources.

Task 3. Technical Evaluation and Conceptual Design Studies:

3a. Thermal Sources - other than nuclear (specifically solar and coal).

3b. Chemical Reactors - This subtask will examine both reforming and methanation reactors. Reactor design requirements shall be determined for application to CHP systems. Various chemical reactor types (adiabatic, isothermal, and recycle) shall be compared on an energy efficiency basis.

3c. Heat Exchanges - The heat exchange requirements for the methanation and reforming processes shall be parametrically examined. Recommendations as to heat exchanger type, sizes and process flows should be developed. A similar analysis should be preformed for condensers.

3d. Catalysts - High activity catalysts shall be evaluated for reforming/methanation reactions, and those identified which are most suitable for CHP applications. Existing data applicable to reaction kinetics should be examined. Guidelines shall be developed for future catalyst research directed toward resolving problems unique to this application.

3e. Pipeline Transmission/Storage - The technical problems associated with the transport of CO/H_2 and CH_4/CO_2 mixtures shall be assessed and the pumping requirements as a function of various design parameters shall be examined.

Task 4. Determine Customer Needs: The critical problem and needs of utility and potential industrial users of thermal energy supplied by chemical heat pipes shall be assessed. System operating modes with the highest user impact shall be identified.

Task 5. Preparation of an Economic Analysis: Using the data from Tasks 1-4, a preliminary economic analysis of selected system operating modes shall be developed.

Task 6. Conceptual Design for a CHP (as modified): Preparation of a conceptual design for a CHP based upon the benzene hydrogenation/cyclohexane dehydrogenation reversible reactions. A preliminary technical and economic analysis shall be performed for this system coupled with near term U. S. primary energy sources, namely light water nuclear reactors, liquid metal fast breeder reactors and low temperature solar sources.

Task 7. CHP Solar Interface (as modified): Critically evaluate the technical problems associated with combining various focused solar concepts with the CHP.

Task 8. Documentation (as modified): Upon completion of Task 7, a final technical report shall be prepared.

PROJECT STATUS:

Technical Progress

Task 1. Process Design - Complete: A flexible package of computer programs has been developed to perform design analyses of methane chemical heat pipes.

A new design concept, the mixed feed evaporator (MFE), has been invented that allows a major improvement in the match of heating and cooling duties. The feed boiler and gas heater functions are combined into a single unit, which results in a decrease in entropy of mixing.

A significant fraction (up to 10%) of the delivered energy can be extracted from a single shaft compressor/expander at the methanotor (user) end of the CHP.

Task 2. Chemical Reactions - Complete:

Methane System - CO_2 addition favors conversion at the methanator (user) end of the CHP while requiring increased reformer heating duty loads and pipeline flow rates. The addition of CO_2 is justified only when high quality (temperature) heat is required at the user end offsetting the drop in energy efficiency from 89 to 91 percent. Increasing the H_2O recycle has essentially the same advantages and disadvantages as CO_2 addition, though the major effect of H_2O recycle is upon catalyst lifetime.

Alternate Reactions - Of the 15 different high-temperature reactions evaluated, the methane reforming couple is most attractive for high-temperature systems. For lower-temperature sources, benzene hydrogenation/cyclohexane dehydrogenation is the best.

Task 3. Complete:

3a. Thermal Sources - The minimum reformation temperature, consistent with the process parameters, is 950 K; this restriction limits consideration of available sources to the pebble bed nuclear reactor and direct coal fired.

3b. Chemical Reactors - Significant improvements are possible for methanators via the use of state-of-the-art techniques, i.e., adiabatic reactor stages with intercoolers. The KFA steam reformer design can be improved and must be modified for domestic USA use. (See Project Number 2.2.2, The Duplex Steam Reformer.)

3c. Heat Exchangers - A trade off between heat exchanger area, cost, and temperature drop has been performed. The issues are primarily investment capital cost versus availability loss, not technical barriers.

3d. Catalysts - Reforming Rachig ring catalysts are state-of-the-art. Lifetime preformance can be improved by the use of H_2O recycle. Flame sprayed catalysts or catalysts with improved support geometrics which allow speedy removal or in-situ regeneration are a general improvement desirable for, but not limited to, the CHP reformer.

3e. Pipeline Transmission/Storage - The technical problems associated with the transmission and storage of CO/H_2 and CH_4/CO_2 mixtures are not insurmountable. Line packing with a $\pm 2 \times 10^6$ newtons/meter^2 variation about 4×10^6 N/m^2 nominal pipeline pressure will yield approximately 5 hours of storage in a 160 km, 1.6 m diameter pipeline, assuming a nominal energy transmission of 1000 Mj/s.

Task 4. Customer Needs - Complete: The best potential application for a chemical heat pipe distributing process heat is the one- and two-shift industrial user for whom the on-site coal based steam generation is too costly when stack clean up equipment is included in the cost. For cases where $T < 800$ K, and the individual user size is below 200 Mj/s, the potential is roughly 80 GW_{th}.

Clearly identified is the lack of process heat market data with regard to:

User geographic location

Energy consumption as a function of temperature, capacity requirements

User duty cycles

Types of fuel presently used

Task 5. Economic Analysis of Selected System Operating Modes - Complete: The cost of delivered process steam is competitive with options such as SNG fired boilers, electrode boilers, and perhaps small coal fired boilers with stack clean up equipment. Applications that are most favorable economically include supplying process steam to small and part-time users; distributed generation of peak electricity, and co-generation of electricity and heat for small users. The chemical heat pipe is marginally competitive with other techniques for on-site thermal energy storage. Depending upon the assumptions made, the CHP can be considered as an alternate to on site generation of process steam for large, continuous users.

Comparing energy transmission alternatives, the major strengths of CHP lie in the middle distances (80-320 km).

For solar CHP applications, the CHP is at a disadvantage due to the large capital cost of a reformer with a capacity factor of 1/3. Peak operation of the methanator is feasible, as its capital cost is not a major factor at the user end.

Task 6. Preparation of a Conceptual Design for a CHP Based Upon the Benzene Hydrogenation/Cyclohexane Dehydrogenation Reversible Reactions - Complete: Analysis of the low-temperature chemical heat pipe (LTCHP) indicates economics and performance characteristics superior to those of the methane-based CHP. Uncertainties which must be resolved experimentally include the degree of dehydrogenation catalyst selectivity, process optimization, and the maximum attainable hydrogenation temperature. The transportation system design must accommodate the relatively high freezing temperatures of benzene (5. 50 C) and cyclohexane (6. 5 C), the fire hazard of these and hydrogen, and the toxcity of benzene.

Task 7. CHP Solar Interface - Complete: The operating characteristics of a concentrating solar thermal source are largely unknown. Diurnal thermal cycling is the minimum period of source temperature variation. The endothermic reactor must be "buffered" from this and other thermal shocks for catalyst longevity.

The nature of the source imposes severe economic capitalization penalties upon the endothermic equipment when compared to continuous operating sources such as the LMFBR and coal-fired dehydrogenators.

Task 8. Documentation: A draft version final report has been rc-ceived.

Technical Problems

The major technical problems associated with this study have been the paucity of specific data. Examples are the detailed geographical characterization of the process heat user market, the duty cycles and the steam temperature requirements. The characteristics of high-temperature solar thermal sources are not clearly specified at present, which limits minimizing the technical effort that can be expended upon Task 7.

Program Management

A majority of the contract goals has been realized. The singular exception is the final documentation, which will be delayed approximately six months from the 9/77 scheduled date. A draft version was received August 19 and distributed to a twelve-member review panel August 30. Ten reviews and an edited copy of the report were returned to G. E. on October 19, 1977.

PROJECT NUMBER: 2.2.2

PROJECT TITLE: Duplex Steam Reformer Development Program

CONTRACTOR: General Electric Company
Energy Systems Program Department
1 River Road
Schenetady, N.Y. 12345

CONTRACT NUMBER: EY-76-C-02-2841

CONTRACT PERIOD: May 1976 - December 1979

CONTRACT AMOUNT: $110,000; Estimated cost at completion $857,000

PREVIOUS CONTRACTS/AMOUNT: Phase 1/$75,000
Phase 2A/$46,000

PROGRAM MANAGER: M. A. McDermott

SANDIA TECHNICAL MANAGERS: T. T. Bramlette, J. J. Bartel

PROJECT SUMMARY:

Objectives

The objectives are to design, fabricate, test, and evaluate a full-scale duplex steam reformer (DSR) tube. Reforming steam produced by nuclear heat has potential industrial applications; the DSR provides double-walled isolation between a potentially radioactive high-temperature nuclear heat source and the industrial process gas. The DSR tube will be fabricated by the Foster Wheeler Development Corporation (FWDC) of Livingston, New Jersey, and tested in the EVA test facility of the Kernforschungsanlage (KFA) in Julich, West Germany.

Tasks

Work on the DSR program has been divided into five phases. Phase 1, Study and Planning, was completed in May 1976. Phase 2A, Duplex Tube Fabrication Feasibility Demonstrating Program, was added to the original program in order to demonstrate the feasibility of the proposed kinetic construction process for fabricating the DSR. Phase 2A was completed on August 15, 1977. The remaining phases of the program are: Phase 2, Test Section Procurement; Phase 3, Steam Reformer Test and Performance Evaluation; and Phase 4, Post Test and Metallurgical Evaluation.

The following tasks have been identified to cover the work in Phases 2, 3, and 4:

Task 1. Program Management: Contract management services, including liaison with KFA, will be provided to ensure that the schedule for the duplex tube delivery to KFA is compatible with the scheduled availability of the EVA test facility.

Task 2. Duplex Tube Procurement: Two duplex steam reformer tubes will be fabricated by Foster Wheeler Development Corporation (FWDC) under subcontract to G.E.; one of these tubes will be shipped to KFA for testing in the EVA facility. This task shall be completed by issuance of a manufacturing report describing the materials used, the processes developed and used, the quality control measures, and a description of the final product.

Task 3. Test Section Assembly and Installation: KFA, under agreement with G.E., shall be responsible for test section assembly and installation, which includes:

Design and fabrication of the adapters to mate the DSR tube with the EVA facility

Design and fabrication of the catalyst to be placed in the DSR tube during the test program

Design and fabrication of the instrumentation to be used to measure the DSR performance characteristics

Assembly of the test section in preparation for the test program.

Task 4. Test Program: KFA has responsibility for preparing the test program specification and obtaining G.E. concurrence with this program. This program shall include testing at three helium inlet temperatures and three steam-methane ratios. Also, the hydrogen permeation rates shall be measured. Pretest predictions will be made which shall include tube temperatures and hydrogen permeation rates.

Task 5. Performance Evaluation: This task covers the evaluation of the metallurgical performance and reformer performance of the DSR tube, and includes:

The preparation of a metallurgical evaluation plan for the duplex tube including pretest and post-test evaluations.

The pretest evaluation of the metallurgical characteristics of the DSR tube. This will include tensile specimen tests and surface finish examination.

Task 6. Engineering: This task includes the following engineering activities to support the manufacture, test, and evaluation of the DSR tubes:

Review and selection of an analytical model for predicting the DSR performance during testing in the EVA facility and performance of sensitivity studies to support the test program.

Performance of the necessary metallurgical engineering to support the manufacture of the DSR tubes. This includes establishing the type of oxide film to be on the tubes, establishing annealing temperatures, and evaluating the effects of cold work and fatigue on the tube performance.

Task 7. Licensing Evaluation: The contractor shall prepare and submit to the U. S. Nuclear Regulatory Commission (NRC) a Preliminary Licensing Submittal (PLS) describing the use of a duplex steam reformer in conjunction with the gas-cooled nuclear reactor in the U. S. The contractor shall also prepare responses to questions raised by the NRC in their review of the PLS.

PROJECT STATUS:

Technical Progress

Work performed during Phase 2A has demonstrated the feasibility of explosively forming the duplex tube assembly.

Technical Problems

Additional work on the welding procedure used to weld the end cap to the outer tube is required to eliminate weld-metal protrusion into the gap between the outer and inner tubes. Also, additional effort is required to determine the proper intermediate annealing temperature for the 12 m duplex tubes to be produced for the KFA tests.

Program Management

Management to date has been satisfactory. Performance, cost, and schedule goals have been met. The current phase of the program was initiated on September 30, 1977.

Publications

1. Kimball, O. F. and Schroeder, J., Duplex Tube Combined Steam Reformer/Intermediate Heat Exchanger Development Program - Phase IIA, Duplex Tube Fabrication Feasibility, Demonstration Program, AES 2841-(1), General Electric, Schenectady, N. Y., May 1977.

2. Bond, J., et al., Design of a Helium Heated Duplex Tube Steam Methane Reformer, ESTD 76-06, General Electric, Schenectady, N. Y., May 1976.

PROJECT NUMBER: 2.2.3

PROJECT TITLE: Alternate Catalyst Development Program

CONTRACTOR: General Electric Company
Energy Systems Programs Department
1 River Road
Schenectady, N.Y. 12345

CONTRACT NUMBER: EY-76-C-02-2926

CONTRACT PERIOD: June 1, 1976 - September 30, 1977

CONTRACT AMOUNT: $69,469

PREVIOUS CONTRACTS/AMOUNT:

PROGRAM MANAGER: M. C. McDermott

SANDIA TECHNICAL MANAGER: James J. Bartel

PROJECT SUMMARY:

Objectives

Task 1. Preparation of alternate catalyst designs for helium gas heated steam reformers. The goal of this task is to evaluate new catalyst designs which offer longer operational life, the potential for in-situ regeneration, higher thermal conductivity, and rapid replacement.

Task 2. Fabrication of the recommended design.

Task 3. Test at KFA in the EVA helium heated reformer test apparatus.

Task 4. Evaluate the test results.

Task 5. Report

PROGRAM STATUS:

Technical Progress

Task 1. Preparation of Alternate Catalyst Designs: Since the completion of a subcontracted Foster Wheeler Development Corporation (FWDC) catalyst design evaluation, G.E. has concluded that the FWDC design should not be pursued.

G.E. considers that the potential performance improvements with an advanced catalyst warrant continuation of this program. A configuration proposed by the ESCOA Corporation has been analyzed and is expected to perform better than the FWDC design. In addition, contacts have been made with research groups who specialize in catalyst development to determine their interest in working with G.E. on developing and proof-testing an improved catalyst for this program.

Task 2 thru 4. See Technical Problems

Task 5. Two technical reports were received:

A. FWDC Report AT 77-3 "Task 1 Report, Design and Evaluation of an Alternate Catalyst for a Helium Heated Steam Reformer," Peter Steiner and Carl Gutterman, January 1977.

B. "Evaluation of Alternate Catalyst Designs for a Helium Heated Methane Reformer," G. P. Sakellaropoulos, June 1977.

Technical Problems

FWDC regards the majority of the technical information contained within Report AT 77-3 and the G. P. Sakellaropoulos review of same as proprietary. After reviewing the technical documentation, and providing the contractor (G.E.) with an opportunity to rescope the work statement, Sandia concluded that the continuation of this work beyond Task 1 is premature. The development and testing of an alternate catalyst should await satisfactory demonstration of the duplex steam reformer (see Project Number 2.2.2).

Management Problems

Due to proprietary considerations and management changes, supporting documentation for Task 1 was six months late. The contract was allowed to expire at the end of GFY 77. Approximately $32,600 was expended of an authorized $69,469.

Publications

See Task 5, Technical Progress.

PROJECT NUMBER: 2.2.4

PROJECT TITLE: Cyclic Catalytic Solar Energy Storage Systems

CONTRACTOR: University of Houston
Houston, Texas 77004

CONTRACT NUMBER: EG-77-C-04-3974

CONTRACT PERIOD: May 1977 to May 1978

CONTRACT AMOUNT: $25,000

PRINCIPAL INVESTIGATOR: W. W. Wendlandt

SANDIA TECHNICAL MANAGER: Reginald E. Mitchell

PROJECT SUMMARY:

Objectives

The Eva-Adam concept of energy storage is a potential method for solar energy utilization in which the steam reforming reaction of methane is carried out at high temperatures with the resultant transmission of the synthesis gas to demand center and then methanation to produce heat. Due to the question of cyclic heat supply at the solar collector, the reforming reactor will be interfaced to a liquid sodium receiver which will contain a thermal storage unit and a heliostat subsystem optimized for this receiver. This preliminary work will optimize the process stages and determine the process parameters at the steam reforming-liquid sodium receiver end. This information will provide not only an indication of the flexibility of the scheme but also establish the range of temperatures, pressures, and compositions to be encountered by the reforming catalyst.

Tasks

Computer programs will be developed to model each of the following steps in the overall process: (a) steam reforming at the liquid sodium-reforming reactor, (b) cooling and water removal, (c) carbon dioxide removal, (d) transmission from the reactor to the demand center, (e) storage, (f) shift reactions, (g) methanation and heat removal, (h) carbon dioxide removal, and (i) transmission back to the reformer reactor.

For each of these steps, equilibrium compositions will be calculated as a function of pressure, reactor temperature, and quantity of heat supplied. The model will be used to compare permutations of the following modes of operation: (a) single-pass operation, (b) steady-state closed-loop operation, (c) isothermal operation, and (d) cyclic operation (expected from current design). The process configuration and operating ranges will be determined for the optimum design.

PROJECT STATUS:

Technical Progress

The computer model of the proposed cyclic solar storage process has been completed. The model, as developed to date, gives equilibrium compositions for all streams as a function of process operating conditions (temperature, pressure, and steam/hydrocarbon ratios). Necessary heat inputs and diverter heat outputs are also calculated. The model may be run in a number of different modes, i.e., (a) isothermal at all stages, (b) single-pass or recycle for the methane feed, (c) non-isothermal-cyclic at the solar plant and/or adiabatic at the demand plant, and (d) with or without interstage processes (i.e., heat exchangers to heat or cool the input and output streams at each plant).

Program Management

The program is progressing satisfactorily with cost and time schedules being maintained at the levels outlined in the contract.

Chemical Heat Pump Projects (TBS 3.0)

The following projects are discussed in this subsection:

3.1.1 Sulfuric Acid/Water Integrated Chemical Energy Storage System

3.1.2 One Substrate Solvate Energy Carrier System for Storage of Solar Energy

3.1.3 The Chemical Heat Pump: A Simple Means to Conserve Energy

PROJECT NUMBER: 3.1.1

PROJECT TITLE: Sulfuric Acid/Water Integrated Chemical Energy Storage System

CONTRACTOR: Rocket Research Corp.
A Division of Rockcor, Inc.
York Center
Redmond, Washington 98052

CONTRACT NUMBER: EY-76-C-03-1185

CONTRACT PERIOD: October 1976 to December 1977

CONTRACT AMOUNT: $287,000

PREVIOUS CONTRACTS/AMOUNT: December 1975 to June 1976
$54,800

PRINCIPAL INVESTIGATOR: E. Charles Clark

SANDIA TECHNICAL MANAGER: Carl C. Hiller

PROJECT SUMMARY:

Objectives

The objectives of this program are to demonstrate the feasibility of using sulfuric acid and water as a chemical energy storage media, to build and test a subscale (100,000 BTU) demonstration system, and to build and test a full-scale pilot plant. The current Phase II program was started in October 1976 and is scheduled to be completed in December 1977.

Tasks

Task 1. System Selection, Detailed Sizing and Scaling Analysis. The sulfuric acid/water chemical energy storage system is intended to be applied to the heating and cooling of buildings. A detailed sizing and scaling analysis was conducted, with the Phase I system approach resulting in storage densities of 120 to 200 btu/lbm of dilute acid. During this phase, the concept of using sulfuric acid as a chemical heat pump was identified. Because this concept results in storage densities in excess of 500 btu/lbm, it has been pursued as the main approach for Tasks 2 through 4 below. Also as a part of this task, an economic study plan and a test plan for Task 4 were generated.

Task 2. Detailed Design, Equipment Selection and System Layout. The system was designed, with detailed drawings and flow diagrams produced. Preliminary laboratory scale separation tests were initiated early in the program to optimize the separation design. Material compatibility tests have been conducted to determine the dynamic effects of the hot concentrated sulfuric acid. In addition, a preliminary safety and hazard analysis of the system has been conducted. At the conclusion of Task 2, a design review will be conducted jointly with DOE and RRC personnel.

Task 3. Fabrication, Assembly and Checkout. The procurement, fabrication and assembly of the system components and hardware have been performed during Task 3.

Task 4. Chemical Energy Storage Operation/Evaluation and Phase III Definition. The integrated system is being tested and the performance evaluated and compared against predictions. The efficiencies of both components and the total system efficiencies will be measured, and corrosive and wear characteristics of the system will be monitored. The program will be concluded with the establishment of the requirements for a full-scale operational system and the recommendations for Phase III.

PROJECT STATUS:

Technical Progress

The program has proceeded largely on schedule. The recombination tests identified an absorption column as being potentially the most cost effective batch recombination approach, and as such it has been chosen for the baseline design. A continuous separation column approach was also identified as technically viable and is being pursued as a backup to the baseline batch concept.

The computerized performance analysis has identified the operating limits of the baseline system design, and will enable analysis of performance results obtained from the demonstration test system.

The demonstration test system has been designed, procured, and assembled, and preliminary checkout operation is now in progress. Concurrent with the latter have been the establishment of the testing program, operating procedure, and safety requirements. Safety requirements and other barriers to implementation of commercial systems are being analyzed as an ongoing effort.

Technical Problems

Minor problems encountered during the procurement of the demonstration facility components resulted in a schedule slip of approximately 3 weeks. This slip had little or no impact on project cost.

Program Management

Management of the program has been entirely acceptable. Delays in component procurement were beyond the control of the principal investigators, and efforts are being made to return the program to its scheduled status. The project is within budget.

Publications

1. Huxtable, D. D., and Clark, E. C., "Sulfuric Acid-Water Chemical Energy Storage System," RRC-76-R-530, Rocket Research Corporation, Redmond, Washington, August 1976.

PROJECT NUMBER: 3.1.2

PROJECT TITLE: One Substrate Solvate Energy Carrier System for Storage of Solar Energy

CONTRACTOR: EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158

CONTRACT NUMBER: SLL No. 87-9118

CONTRACT PERIOD: May 1977 - May 1978

CONTRACT AMOUNT: $120 K

PREVIOUS CONTRACTS/AMOUNT: None

PRINCIPAL INVESTIGATOR: P. O'D. Offenhartz and J. P. Pemsler

SANDIA TECHNICAL MANAGER: R. W. Mar

PROJECT SUMMARY:

Objectives

The objectives are to find salt-methanol combinations that are thermodynamically and kinetically suitable for a chemically driven heat pump designed to store solar thermal energy, and to provide preliminary design information for chemical heat pump storage systems.

Tasks

Task 1. Preliminary Enthalpies and Entropies of Salt (Substrate) - Gas (Energy Carrier) Reactions: Initial Selection of Substrates: The reactions of various salts with CH_3OH will be studied, and correlations among enthalpies, entropies, and stoichiometries will be developed. These correlations, in combination with available data on the reactions of these salts with other polar solvents, will be used to optimize the salt reactant.

Task 2. Pressure-Temperature-Composition Diagrams: For each attractive salt, the solvate composition will be determined as a function of temperature and pressure. Temperatures will be varied in the range -30 to 150°C, pressures in the range 0.01 to 1 atm. Studies will be made by thermogravimetric analysis (TGA).

Task 3. Gas-Salt Reaction Kinetics: The rate of temperature increase or decrease will be varied to obtain quantitative estimates of gas-salt reaction kinetics. In suitable cases, the kinetics of complex formation and decomposition will be studied in more detail, by means of TGA with linear temperature scan and with a derivative computer. Rate equations will be obtained which include the effects of temperature, gas pressure, and solid-phase composition.

Task 4. Heat-Transfer Coefficients: The rate of heat flow through the solid complexes will be measured using thermal cells. The influences of effective density, solid-phase composition, gas pressure, and mean temperature will be studied.

Task 5. Engineering Scoping and Economic Analysis: The thermodynamic and kinetic data obtained in the previous tasks will be used to define the scope of the system and to obtain cost estimates for various storage configurations. Particular attention will be paid to the possibility of designing an economically feasible, long-term (seasonal) storage system.

Task 6. Side Reactions and Effects of Chemical Purity: Compounds will be checked for long-term stability and freedom from irreversible side reactions, as evidenced by hysteresis or irreproducibility in the TGA temperature-pressure-composition curves after the compounds have been subjected to accelerated aging at the highest temperature (150°C). The aged samples of solvate will be fully decomposed at higher temperatures, and the effluent gases analyzed with gas chromatography for products from side reactions. Possible changes in kinetics due to sintering (decrease in specific surface area) will be examined.

PROJECT STATUS:

Technical Progress

Task 1. An experimental apparatus was designed, assembled, and checked for use in Tasks 1 and 2. Preliminary screening experiments have been completed; the approximate temperature-composition profiles of twenty-one inorganic salts were measured at 0.1 atm methanol. Five promising salts were identified and chosen for continued study: $MgCl_2$, $FeBr_2$, $CoBr_2$, $CaBr_2$, and $CaCl_2$.

Task 2. Experiments at 0.02 atm methanol with the five salts selected are in progress.

Task 3. A comprehensive literature survey of kinetic studies which pertain to hydrated salts has been completed. Very little insight was provided to the problem at hand, and it is concluded that our understanding of methanolated salt reaction kinetics will not benefit greatly from previous work on hydrates. Preliminary observations made during Task 2 experiments suggest potentially slow kinetics at the lower temperatures.

Technical Problems

No insurmountable technical problems have been encountered. The identification of suitable salts for continued study took longer than anticipated; as a result, the rate at which scheduled milestones are reached may be slowed.

Program Management

In view of the fact that (1) so few salts form methanolates in the appropriate temperature-pressure range and (2) reaction rates may be slow, a suitable methanolate may not be found. In that event, EIC should be given the freedom to expand their charter to include such things as ammoniates and hydrates. The subcontractor has demonstrated a thorough understanding of chemical heat pump systems, both from an engineering and scientific standpoint. It is our opinion that the successful development of a chemical heat pump system rests not with finding the optimum chemical system, but with clever hardware and system design.

Publication

Presentation at the TES Contractors Information Exchange Meeting, Gattinburg, Tennessee.

PROJECT NUMBER: 3.1.3

PROJECT TITLE: The Chemical Heat Pump: A Simple Means to Conserve Energy

CONTRACTOR: Chemical Energy Specialists
1310 Logan Avenue
Suite C
Costa Mesa, California 92626

CONTRACT NUMBER:

CONTRACT PERIOD: August 1 to December 31, 1977

CONTRACT AMOUNT: $40,000

PREVIOUS CONTRACTS/AMOUNT: ERDA contract, $62,000

PRINCIPAL INVESTIGATOR: Leonard Greiner

SANDIA TECHNICAL MANAGER: Robert W. Carling

PROJECT SUMMARY:

Objectives

The program objectives have been to continue development of the chemical heat pump by building working models using $MgCl_2 \cdot xH_2O$ as the storage material. No specific tasks were designated.

PROJECT STATUS:

Technical Progress

A simplified version of the collector-absorber has been conceptualized. Experiments using a glass vaporizer have been designed and conducted.

New absorbers have been built to reduce leaks in the system. Experiments using $MgCl_2 \cdot xH_2O$ as the absorber material have centered on the effects of bed thickness and the problems due to the production of HCl during dehydration. Investigation of other absorber materials has been started; the most promising appears to be $LiCl \cdot xH_2O$

Technical Problems

The most serious problem is the production of HCl during dehydration of $MgCl_2 \cdot xH_2O$. The HCl produced attacks the container and may prevent recharging of the system. The most promising alternative is $LiCl \cdot xH_2O$; however, all lithium salts are very expensive.

Program Management

Based on the work statement and the contractual arrangement, CES is on schedule and meeting costs.

Generic Research Projects (TBS 4.0)

The following projects are discussed in this subsection:

4.1 Heat Transfer in Packed Beds at Low Reynolds Number

4.2 The Kinetics of Dissociative Chemical Reactions in Thermochemical Energy Storage

4.3 Development of a Long-Life High-Temperature Catalyst for the SO_2/SO_3 Energy Storage System

4.4 Development of Ammoniated Salts Thermochemical Energy Storage Systems

4.5 Sandia Laboratories In-House Research

PROJECT NUMBER: 4.1

PROJECT TITLE: Heat Transfer in Packed Beds at Low Reynolds Number

CONTRACTOR: Martin Marietta Corporation
Colorado State University

CONTRACT NUMBER: 87-8253

CONTRACT PERIOD: March 1, 1977 to September 30, 1977

CONTRACT AMOUNT: $14,472

PREVIOUS CONTRACTS: None

PRINCIPAL INVESTIGATOR: F. C. Prenger

SANDIA TECHNICAL MONITOR: R. M. Green

PROJECT SUMMARY:

<u>Objectives</u>

The objectives are:(1) to determine the heat transfer characteristics of a packed bed salt reactor through which a gas is flowing (of specific interest are the effective bed conductivity and solid/gas heat transfer coefficient at imbedded surfaces), and (2) to correlate the data for use in the MITAS II math model.

<u>Tasks</u>

Task 1. Setup test apparatus and check out its operation.

Task 2. Formulate a mathematical model of the test system for data correlation purposes.

Task 3. Measure the characteristics of the test beds using sand and salt ($CaCl_2$).

Task 4. Collect heat transfer data by operating the test apparatus with selected working substances.

Task 5. Correlate the heat transfer data.

PROJECT STATUS:

Technical Progress

All of the tasks in this program have been completed by the contractor, and a draft final report has been submitted.

The data obtained were correlated without the usual assumption of equal solid and gas temperatures, thus extending the applicability of the data to low Reynold's numbers. Satisfactory correlations of the data were obtained, thus allowing the direct use of the results in the MITAS II model of the reacting salt system. Sensitivity studies and error analyses were performed to complete the study.

Technical Problems

There were no technical problems reported by the contractor during the last six months (or during the duration of the program).

Program Management

The contractors performance on this project during the last six months has been excellent. The work performed and the results obtained are of the highest quality.

Publications

1. Prenger, F. C., "Heat Transfer in Packed Beds at Low Reynolds Number," MCR-77-438, Martin Marietta Corp., Denver, Colorado, October 1977.

PROJECT NUMBER: 4.2

PROJECT TITLE: The Kinetics of Dissociative Chemical Reactions in Thermochemical Energy Storage

CONTRACTOR: Professor Z. A. Munir
University of California
Davis, California

CONTRACT NUMBER: SLL No. 18-0438

CONTRACT PERIOD: July 1977 - July 1979

CONTRACT AMOUNT: $125 K

PREVIOUS CONTRACTS / AMOUNT: None

PRINCIPAL INVESTIGATOR: Professor Z. A. Munir

SANDIA TECHNICAL MANAGER: R. W. Mar

PROJECT SUMMARY:

Objectives

The basic objective is to provide a thorough understanding of the kinetics of dissociation and association of selected reactions for use in thermochemical storage schemes.

Tasks

Task 1. Identification of attractive chemical reactions for thermochemical energy storage systems and evaluation of existing data.

Task 2. Selection of systems for investigation.

Task 3. Identification and selection of experimental methods.

Task 4. Experimental kinetics.

PROJECT STATUS:

Technical Progress

To assist in the selection of reactions for continued study, a comprehensive computer-aided literature search is under way to identify and classify thermodynamic and kinetic properties of several families of compounds which can be used in thermochemical storage systems. A master table of all potentially useful chemical systems will be prepared, which will include the current understanding of their thermodynamic and kinetic properties as well as the degree of reliability of the information presented.

Task 3 has been initiated. Thermogravimetric analysis techniques will be used in the experimental portion of this study. Equipment items have been identified and ordered, and the design and fabrication of the apparatus are under way.

Technical Problems

No problems have surfaced.

Program Management

This project is proceeding satisfactorily; Prof. Munir has assigned several graduate students to this effort. The first phase of this study will complement the RRC reaction screening survey. We are going to get a fresh outlook on the TES problems, as none of the UCD people have previously been involved with TES technology development.

PROJECT NUMBER: 4.3

PROJECT TITLE: Development of a Long-Life High-Temperature Catalyst for the SO_2/SO_3 Energy Storage System

CONTRACTOR: Rocket Research Corporation
Redmond, Washington 98052

CONTRACT NUMBER: 87-9119

CONTRACT PERIOD: May 1977 - December 1979

CONTRACT AMOUNT: $320,247

PREVIOUS CONTRACTS/AMOUNT:

PRINCIPAL INVESTIGATOR: Eckart W. Schmidt

SANDIA TECHNICAL MANAGER: Bernice E. Mills

PROJECT SUMMARY:

Objectives

The objective is to develop a new, more durable catalyst for the reversible SO_2/SO_3 reaction:

$$SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3$$

This reaction has been identified as one of the more promising reversible chemical reactions for the storage of thermal energy. The ultimate goal is a catalyst capable of maintenance-free operation for 30 years at the design temperature of 1089 K (1500°F).

Tasks

For convenience of scheduling and monitoring program status, the program is subdivided into four technical tasks.

Task 1. Laboratory Evaluation: This task involves a laboratory evaluation of commercial catalysts and the development of a standard activity test. Existing catalyst samples will be solicited from catalyst suppliers and analyzed to identify the degradation mechanism at above-nominal temperatures.

Task 2. Catalyst Development: The major effort of the program is conducted in this task. The catalyst development task consists of matching a proper catalyst substrate with an active metal. The catalyst substrate shape will determine the type of reactor to be used. Three catalyst substrate types will be investigated:

Granular or pelletized supported catalyst

Fluidized bed powdered catalyst

Molten catalyst

Eleven candidate active metals have been identified during the pre-contract survey. Of the more than 50 catalysts, five will be selected for more detailed characterization and short-term durability tests.

Task 3. The economics of catalyst preparation and availability of raw materials will be surveyed under Task 3. The trade off between a more durable, expensive catalyst and a less durable, inexpensive catalyst will be quantified. Other possible commercial uses for the new catalyst will also be identified.

Task 4. Accelerated Life Testing: The catalyst selected in Task 2 and justified for economic viability in Task 3 will be subjected to a six-month accelerated life test in this task. Samples will be withdrawn periodically during the test to monitor the rate of catalyst degradation. Toward the end of the six-month test, interim data will be assembled and DOE/SLL recommendations will be requested on whether the test should be terminated at six months as planned or if additional life should be demonstrated by extending the test beyond six months.

Task 5. Reporting and Review: Reporting and program review duties are covered under Task 5.

PROJECT STATUS:

Technical Progress

Task 1. Commercially available catalyst samples have been obtained. Seven of these have been analyzed by their emission spectra and twenty-one by a standardized analytical method for non-noble metal catalysts. A standard activity test has been defined, and an activity test reactor is under construction. A test matrix and a method of data reduction have been identified.

Task 2. Examination of phase diagrams indicates that even the most favorable eutectics available as a solvent for a molten catalyst have too high a melting point. Therefore, the supported catalyst is the type chosen for further study.

Technical Problems

There have been delays in the program because of equipment problems. The oxygen analyzer needed for the activity test was found to be incompatible with SO_3, and the cell must be replaced. The gas chromatograph with the gas density balance, which is also necessary for the activity test, was received without the necessary thermal conductivity detector.

Program Management

The only slip in the schedule was caused by equipment problems rather than fundamental flaws in the program, and should be rectified soon. There are no cost or technical problems.

PROJECT NUMBER: 4.4

PROJECT TITLE: Development of Ammoniated Salts Thermochemical Energy Storage Systems

CONTRACTOR: Martin Marietta Aerospace Corporation
Denver Division, P. O. Box 179
Denver, CO 80201

CONTRACT NUMBER: EY-76-6-03-1229

CONTRACT PERIOD: February 1, 1977 to September 30, 1977

CONTRACT AMOUNT: $191,548

PREVIOUS CONTRACTS/AMOUNT: Phase I of Current Program $250,000

PRINCIPAL INVESTIGATOR: F. A. Jaeger

SANDIA TECHNICAL MANAGER: R. M. Green

PROJECT SUMMARY:

Objectives

The program objectives are to:

1. Demonstrate the feasibility of using paired ammoniated salts for thermochemical energy storage systems.

2. Develop a computer model for predicting the performance of the system.

3. Obtain additional information on the physical properties of the salts.

4. Determine the effect of various impurities on the salt performance.

5. Study various reactor designs.

6. Define any follow-on effort.

Tasks

Task 1. Modeling: Formulate a computerized mathematical model for predicting the performance of thermal storage systems using ammoniated salts.

Task 2. Coupled Reactions: Design, build and test a laboratory scale thermal storage system.

Task 3. Additional Salts Information: Obtain theoretical densities on each of the three $CaCl_2$ ammoniates. Determine the effects of association/dissociation cycling on each of the ammoniates in the free (10 cycles) and constrained volume conditions. Determine particle size distribution at 0, 1, 5, 10, 20, 50 and 100 cycles in the constrained volume test. Determine the surface area of the six ammoniates after 0, 50, and 100 cycles.

Task 4. Moisture Effects Evaluation: Determine the effect of 1 to 6 percent moisture in the salt on the reaction kinetics of one ammoniate of each salt.

Task 5. Economics: Determine the economics of the fixed bed reactor using the data generated in Tasks 1 through 4.

Task 6. Alternate Bed Configuration - Fluidization: Analyze the effect of fluidization on performance of reversible thermal storage systems. Design and fabricate a small scale reactor to determine gas velocity required to fluidize a salt bed. Calculate power requirements for fluidization.

Task 7. Alternate Bed Configuration - Moving Salt and High Flow Fixed Bed: Prepare schematic flow diagrams, analyze performance and investigate potential areas of application of these concepts.

Task 8. Planning Phase 2: Revise the Phase 2 plan presented in the Phase 1 report.

Task 9. Heat of Reaction Confirmation.

Task 10. Effect of Non-Aqueous Impurities: Determine probable impurities in commercial grades of $CaCl_2$ and $MgCl_2$; prepare samples; determine the effect on the reaction kinetics of three ammoniates of $CaCl_2$ and $MgCl_2$.

PROJECT STATUS:

Technical Progress

As of September 30, 1977 this phase of the program ended (except for the submission of the final report), with the contractor indicating the satisfactory completion of all the tasks. A task-by-task summary of the accomplishments of the past six months follows.

Task 1. Performance Modeling: An analytical model of the reactor/heat exchanger system has been formulated for use with the MITAS II computer code. This model is to be used to make system performance predictions for design studies and experimental data analysis. Due to problems which arose with the application of the model to the MITAS II code, there was not sufficient time to verify the adequacy of the model by comparison with experiments; this must be delayed until Phase II. Initial computer runs indicate that the results are reasonable and that the required computer time is not excessive.

Task 2. Cyclic Testing of Coupled Reactions: The following test matrix has been completed; in all cases the low-temperature reactor was run with $CaCl_2 \cdot 8\ NH_3$.

High Temperature Salt	Cycles
$MgCl_2 \cdot 6\ NH_3$	20
$MgCl_2 \cdot 2\ NH_3$	38
$MnCl_2 \cdot 6\ NH_3$	20
$MgCl_2 \cdot 2\ NH_3$	30

The experiments carried out in this task have indicated no degradation of performance with cycling. In addition to verifying the coupled reaction concept, these experiments also illustrated system operation in the cooling mode (low-temperature reactor).

Task 3. Additional Salt Information: The cyclic testing of all the ammoniates of $MgCl_2$ and $CaCl_2$ has been completed, and the required physical characteristics determinations have been made. The only surprise observed in these tests was the large volume change of $CaCl_2$ on initial ammoniation. In a constrained volume, this large change results in the formation of a rock-like substance.

In general, the cycling resulted in very little change in the physical characteristics of the salts.

Task 4. Effects of Moisture: The objectives of this task were satisfactorily completed. It was shown that small amounts of moisture (less than 6 percent) will not significantly affect the reaction rates of either the $MgCl_2$ or $CaCl_2$ ammoniated salts.

Task 5. Economics: An economic system study of an ammoniated salt storage system has been completed. The application was energy storage for feedwater heating for a 50 and 100 MW_t power plant. Comparison was made with a sensible heat system using oil in the same application. Results indicate that the ammoniated salt system is competitive with the oil system in this application.

Task 6. Alternate Bed Configuration - Fluidization: The design of a six-inch diameter fluidized bed reactor was completed. Its construction, however, was halted due to excessive cost, and the experiments were run in an existing two-inch reactor. The results have not yet been reported.

Task 7. Alternate Reactor Design: Two alternate reactor design concepts have been studied: a fixed bed using forced gas flow and a fluidized bed reactor with solids transport to-and-from the reactor and storage bins. It appears that only schematic sketches of these systems will be done for this task.

Task 8. Planning for Phase 2: A Phase 2 proposal has been submitted which supports the heating and cooling application funded by DOE Solar Heating and Cooling R&D Branch.

Task 9. Heat of Reaction Confirmation: This task is complete. The heats of reaction of the ammoniated salts of interest have been either confirmed or determined.

Task 10. Effects of Non-Aqueous Impurities: No substantial effects on the reaction kinetics of $CaCl_2$ were observed in the presence of air or $CaSO_4$.

Technical Problems

During the past six months the major technical problems have been associated with development of the performance model. The major problem was excessive computer time requirements. Extensive modifications were made to the model, but software incompatabilities between it and the MIDAS II code prevented proper running. After spending much programmer time on the problem, the contractor ran out of money and work was stopped. An additional $4K was provided so that the contractor could complete work on the model. The software bug was finally corrected and the model exercised on the MIDAS II code. Time and funding only allowed preliminary checkout of the model; the results, however, look good and additional work will be carried out in Phase II.

The work in Task 2 also was beset with some problems. The major problem was not enough time to complete the scheduled work due to an underestimate of the time needed to carry out a reaction cycle. A request for additional funds was made by the contractor. This request was denied after a review of the available data indicated that the experimental procedure was ill-conceived and that the value of the data was limited. This will be discussed more fully in the next section.

Program Management

The contractor's performance during the past six months was, in general, acceptable. Several areas have stood out, however, as having had a lower quality of work. This has indicated the need to more closely monitor the contractor's work. In the future we plan to have more frequent technical reviews and closer communication.

Publications

1. Progress Report - 3/76 to 9/76 - Development of Ammoniated Salts Thermochemical Energy Storage Systems - Phase I Initial Assessments - Final Report, September 24, 1976, Contract No. E (04-3)-1229, Martin Marietta Corporation, Denver, Colorado.

PROJECT NUMBER: 4.5

PROJECT TITLE: Sandia Laboratories In-House Research

CONTRACTOR: Sandia Laboratories

CONTRACT NUMBER:

CONTRACT PERIOD: September 1976 to September 1977

PRINCIPLE INVESTIGATORS: R. W. Bradshaw, R. W. Carling, D. M. Haaland, J. J. Bartel

SANDIA TECHNICAL MANAGER: R. W. Mar

PROJECT SUMMARY:

Objectives

This activity consists of several studies with the objectives of complementing subcontractor activities and/or gaining the technical expertise and knowledge required for program management and/or conducting research which is long-term and risky in nature. Specific in-house research programs during this reporting period include:

Catalyst Research: To complement and support anticipated development efforts (benzene/cyclohexane concept) and provide a basis for program management decisions regarding hydrogenation/dehydrogenation reactions.

Materials Selection for SO_x TES Systems: Assess the availability of metallic alloys and coatings for the conservation of high-temperature sections of SO_x TES systems.

Hydrated Salt Chemistry: Perform thermodynamic and kinetic measurements on hydrated salts and related analogues, which are potential candidates for TEST applications.

Thermochemical Studies: Provide thermochemical laboratory support to activities of interest in the National Thermal Energy Storage Program.

Sulfur Containing Salt/Alloy Compatibility: Provide a preliminary analysis of material selection problems for sulfur-containing salt systems.

PROJECT STATUS:

Technical Progress

Catalyst Research--During this reporting period, a literature survey of catalytic hydrogenation and dehydrogenation reactions was conducted to start a catalyst research program in support of the cyclohexane/benzene low temperature chemical heat pipe (LTCHP) system to be studied by the General Electric Company. A variety of experimental catalytic surface analysis techniques were investigated, and infrared spectroscopy was selected as the technique for conducting a basic mechanistic study of catalytic processes. Initially, infrared studies of high surface area catalysts will be undertaken to elucidate catalytic mechanisms. For example, although the dehydrogenation of cyclohexane on catalysts has been studied extensively, there is still some controversy as to the rate-determining step. Although most previous work points to the initial formation of cyclohexane as rate determining, limited infrared data and the effects of bimetallic alloy catalysts suggest that the desorption of C_6H_6 is rate limiting. Because alloying of the catalyst is one means of increasing selectivity, a study of catalytic mechanisms could play an important role in the modification of catalysts for greater selectivity. It is proposed that infrared surface work be extended to include studies at higher temperatures and investigations of alloy catalysts. The program will begin with available infrared spectrophotometers. Auger electron spectroscopy and ESCA will be used as complementary techniques where necessary. Later, these studies will be extended to more sophisticated optical methods of surface analysis such as Fourier transform spectroscopy.

This program has only recently been started, and to date no experiments have been completed. However, the required chemicals, catalysts, catalyst supports, and infrared accessories have been ordered. In addition, a sophisticated infrared sample cell has been designed and submitted to the glass shop for construction.

Materials Selection for SO_x TES Systems--A literature search has been conducted using the computerized DIALOG system at SLL along with supplementary manual searches. Specific data on high-temperature SO_2/SO_3 environments are sparse, but it appears that existing alloys designed for service in gas turbines or chemical processing should be suitable except possibly at the highest temperatures. A Sandia Laboratories report summarizing these findings will be issued in the winter quarter of FY78. A number of stainless steels (e.g., 304, 310, 316, and 321) and Inconel-type alloys (e.g., 800, 601, 671, and X-750) have been obtained for testing. Coated alloys will be procured during autumn quarter FY78. Three tubular furnaces and associated temperature and gas composition controls are being set up to carry out the test matrix. Additional electrical power and a gas cylinder shed must be installed before active tests begin. The plant engineering division is constructing these facilities at present.

Hydrated Salt Chemistry--Vapor pressure measurements on the following equilibria have now been completed:

$$MgCl_2 \cdot 6H_2O(S) = MgCl_2 \cdot 4H_2O(S) + 2H_2O(g) \quad (1)$$

$$MgCl_2 \cdot 4H_2O(s) = MgCl_2 \cdot 2H_2O(s) + 2H_2O(g) \quad (2)$$

Vapor pressures from reaction (1) were found to agree with results from previous investigations. Reaction (2), which is the prime candidate for use in the Chemical Energy Specialists' heat pump application, had not been measured previously. Vapor pressures were determined from 293 to 403 K on the tetrahydrate/dihydrate equilibrium. A third law thermodynamic analysis of both equilibria yielded values for ΔH_{298} of 15.1 Kcal per mole H_2O for reaction (1) and 16.5 Kcal per mole H_2O for reaction (2). These can be compared to enthalpies of reaction which are calculated from calorimetrically determined enthalpies of formation, 13.9 and 16.2 Kcal respectively.

Preliminary results suggest significant kinetic problems exist for the $MgCl_2 \cdot xH_2O$ reaction systems; therefore, the suitability of $MgCl_2$ in chemical heat pump systems is in question and must be carefully evaluated. Anomolous behavior was observed when studying reaction (2). After being taken to temperatures above 360 K the reaction would not re-equilibrate at lower temperatures. In other words, while it may be possible to charge the system, reliable and consistent discharging may be an insurmountable problem for a chemical heat pump application. The occurrence of extraneous reactions is suspected. Future work characterizing the gases and solids at selected temperatures will assist in confirming the above conclusion derived from the vapor pressure measurements.

Thermochemical Studies--At the request of Dr. R. Richter of Xerox Electro-Optical Systems, the melting point, melting behavior, and enthalpy of fusion of a ternary salt (64% LiF-30% MgF_2-6% KF by mole) have been determined by differential scanning calorimetry. This salt was a sample from a Xerox thermal energy storage experiment. The melting point was 979 K and the enthalpy of fusion 120 cal gm^{-1}. The salt does not appear to be at the exact eutectic composition, as a minor heat effect was observed at $\sim$910 K.

Sulfur Containing Salt/Alloy Compatibility--The inherent high-energy densities of several sulfur-oxygen containing salts (e.g., NH_4HSO_4, Na_2SO_4, $Na_2S_2O_7$) indicated that the salts may be promising energy storage chemicals in both reacting and non-reacting systems. However, these chemicals are generally agressive; consequently, containment and compatibility are important considerations which must be addressed. Compatibility between commercially available alloys and these salts is being experimentally assessed. To date, a non-flowing isothermal test apparatus has been assembled and checked out. The first test matrix includes $NaHSO_4$ which can be successively decomposed to $Na_2S_2O_7$ and Na_2SO_4 by the loss of H_2O and SO_3. The alloy test matrix includes: (1) A515, a low carbon steel; (2) 304 stainless, (3) Ni-20 Cr-5Al, a high temperature corrosion resistant alloy; and (4) nickel 200, 99.5% Ni. Tentative conclusions to date are: (1) Ni based alloys are subject to serious chemical attack, (2) all alloy systems were noticeably affected within a short period of time, and (3) the Na-S-O ternary system is very complex with the existence of numerous ternary compounds and stoichiometry ranges.

TEST PROGRAM MANAGEMENT (WBS 1.0)

The discussion of program management activities has been structured to be consistent with the TEST Program Work Breakdown Structure (WBS) shown in Figure 12.

Program Planning (WBS 1.1)--A draft of the FY78 Annual Operating Plan was prepared and submitted to ERDA Headquarters for review on September 8, 1977.

Review and Evaluation (WBS 1.2)--During this reporting period, the following projects were reviewed:

2.2.1 General Electric/Corporate Research Division

A brief discussion of the final report was given at GE on August 18, 1977, and the document was submitted for formal review. Attendees were H. Vakil and J. Comley, GE/CRD; and J. J. Bartel and T. T. Bramlette, SLL.

2.2.2 General Electric/Energy Systems Program Department

The duplex steam reformer program was reviewed at DOE Headquarters on April 7 and 8, 1977. A tentative plan of action for a program to be supported jointly by DOE/Nuclear and DOE/STOR was formulated. Attendees were J. Hock, D. Golibersuch, M. A. McDermott, J. Bond, O. Kimball, J. Bast, and A. Kabretz, GE; J. Swisher, C. J. Swet, R. Reeves, and K. Laughon, DOE; P. Graf, TRW; and J. J. Bartel and R. E. Mitchell, SLL.

2.2.3 General Electric/Energy Systems Program Department

The work completed on the first task of this program was discussed on August 18-19, 1977, and possible redirected work considered. The program was cancelled subsequently. Attendees:

M. A. McDermott, GE; G. Sakellaropoulos, consultant; and J. J. Bartel and T. T. Bramlette, SLL.

3.1.1 Rocket Research Corporation

Progress since the last review and the test plan for the closed loop subscale test facility were discussed on September 21, 1977. Minor modifications to the test plan were agreed upon. Attendees: D. D. Huxtable and E. C. Clark, RRC; and T. T. Bramlette, C. C. Hiller, and W. G. Wilson, SLL.

3.1.3 Chemical Energy Specialists

Progress for the first two months of contract was reviewed on September 12, 1977, at CES. Topics considered included current absorber design, modelling activities, and potential problems associated with HCl formation. Attendees: L. Greiner, CES; and R. W. Carling, SLL.

4.1 Martin-Marietta/Colorado State University

Experimental equipment was described and preliminary data were presented on April 26, 1977, at Martin Marietta. No modifications to planned program were suggested. Attendees: Coyne Prenger, C. Hall, and F. Jaeger, MM; C. J. Swet, DOE; and R. M. Green, and T. T. Bramlette, SLL.

At a meeting at Martin Marietta on September 2, 1977, all tasks were reported to be nearing completion with no difficulties encountered or anticipated. Attendees: C. Prenger and F. Jaeger, MM; and R. M. Green and T. T. Bramlette, SLL.

4.4 Martin-Marietta

At a meeting at Martin Marietta on April 26, 1977, the program was reported to be proceeding on schedule. Potential change in emphasis to chemical heat pump storage was discussed. F. Jaeger replaced C. Hall as program manager. Attendees: F. Jaeger, C. Hall, T. Howerton, and S. Podlaseck, MM; C. J. Swet, DOE; and R. M. Green and T. T. Bramlette, SLL.

At a subsequent meeting at Sandia Laboratories, Livermore, on July 1, 1977, it was reported that the program was progressing satisfactorily.

At a meeting at Martin Marietta on September 2, 1977, two major problems were discussed. Data of questionable utility were presented from coupled reactor experiment; further testing was deemed unwarranted. Problems with math modelling program were discussed, and several courses of action were considered. Attendees: F. Jaeger, T. Howerton, S. Podlaseck, MM; R. M. Green, and T. T. Bramlette, SLL.

In addition to the above formal program reviews, numerous meetings were held during the reporting period for various reasons, e.g., proposal presentations, informal program reviews, and information exchange. A list of these activities is given in Table II.

Presentations made by Sandia personnel during this period are given in Table III.

Procurement (WBS 1.4)--Generally, the procurement process proceeds sequentially as follows:

1. Work statement requested by SLL
2. Work statement received by SLL
3. Work statement reviewed by SLL
4. Work statement revised by contractor
5. Work statement accepted by SLL
6. Work statement approved by ERDA/STOR
7. Procurement initiated
8. Procurement complete; contract awarded
9. Work in progress

The current procurement status of all subcontracts anticipated for FY77 funding is illustrated in Figure 14.

TABLE II

SUMMARY OF MEETINGS ATTENDED BY TEST PROGRAM PERSONNEL

Date	Location	Company	Attendees	Purpose
May 11, 1977	SLL	Rocket Research Corp.	D. D. Huxtable, RRC E. Schmidt, RRC R. W. Mar, SLL B. G. Mills, SLL T. T. Bramlette, SLL	Discuss SO_2/SO_3 catalyst program
May 12, 1977	SLL	Rocket Research Corp.	D. D. Huxtable, RRC R. Smith, RRC P. J. Eicker, SLL R. W. Mar, SLL T. T. Bramlette, SLL	Discuss NSF reaction screening program and develop statement of work and interfaces for RRC/SLL extended storage study for solar thermal applications
May 13, 1977	SLL	Rocket Research Corp.	D. D. Huxtable, RRC C. Clark, RRC C. C. Hiller, SLL R. W. Mar, SLL T. T. Bramlette, SLL Chin Fu Tsang, LBL	Discuss H_2SO_4 heat pump program
June 17, 1977	CES	Chemical Energy Specialists	L. Greiner, CES R. W. Mar, SLL R. W. Carling, SLL	Discuss statement of work
June 17, 1977	SLL	Olympic Engineering	J. Brunstrom, OE J. Jacobson, OE C. Ripley, OE T. T. Bramlette, SLL S. Niemczyk, SLA	Discuss possible joint program with Australians to develop ammonia based solar plant
June 27, 1977	JPL	Jet Propulsion Lab	W. Owen, JPL R. Turner, JPL P. Eicker, SLL T. T. Bramlette, SLL	Information exchange
June 30, 1977	LASL	Los Alamos Scientific Laboratory	E. Kaufmann, LASL R. W. Peterson, LASL S. Niemczyk, SLL T. T. Bramlette, SLL	Discuss potential environmental problems associated with reversible chemical reaction storage and transport systems
July 15, 1977	LBL	Lawrence Berkeley Laboratory	S. Lynn, LBL A. Foss, LBL J. Dayan, LBL R. E. Mitchell, SLL T. T. Bramlette, SLL	Discuss FY 78 program

TABLE II (continued)

Date	Location	Company	Attendees	Purpose
July 28, 1977	ERDA	ERDA	R. W. Mar, SLL W. G. Wilson, SLL	Area Managers meeting
August 1, 1977	SLL	Rocket Research Corp	D. D. Huxtable, RRC R. Smith, RRC R. W. Mar, SLL C. C. Hiller, SLL P. J. Eicker, SLL	Discuss H_2SO_4 and extended storage programs
August 24, 1977	SLL	Lawrence Berkeley Laboratory	S. Lynn, LBL A. Foss, LBL J. Dayan, LBL R. W. Mar, SLL R. Bradshaw, SLL B. Mills, SLL T. T. Bramlette, SLL J. J. Iannucci, SLL	Discuss SO_2/SO_3 program and related materials problems
Sept. 9, 1977	SLL	Brookhaven National Laboratory	R. W. Mar, SLL F. Salzano, BNL	Discuss TEST program
Sept. 9, 1977	SLL	Lawrence Berkeley Laboratory	S. Lynn, LBL J. J. Iannucci, SLL T. T. Bramlette, SLL	Discuss LBL program
Sept. 19, 1977 Sept. 20, 1977	GE/CRD UOP	General Electric UOP	D. Haaland, SLA J. J. Bartel, SLL H. Vakil, GE UOP Personnel	Review of GE/UOP chemical heat pipe proposal
Sept. 27, 1977	AI	Atomics International	T. Springer, AI J. Rose, AI W. Thompson, AI J. J. Iannucci, SLL	Discuss SLL extended storage activities
Sept. 28-Oct. 1	Gatlinsburg, Tenn.	Sandia	R. W. Mar, SLL W. G. Wilson, SLL T. T. Bramlette, SLL	Annual review of TEST program

TABLE III

PRESENTATIONS BY TEST PROGRAM PERSONNEL

April 27, 1977	R. W. Mar T. T. Bramlette J. J. Bartel B. E. Mills M. C. Nichols	"Overview of the Thermochemical Energy Storage Program"	American Ceramic Society Meeting, Chicago, Ill.
June 13, 1977	R. W. Mar T. T. Bramlette	"Thermochemical Energy Storage and Transport"	American Nuclear Society Meeting, New York, N. Y.
Sept. 15, 1977	T. T. Bramlette	"The Chemical Heat Pump Storage Program - An Overview"	Second Heat Pump Information Exchange Meeting, National Bureau of Standards, Maryland.
Sept. 30, 1977	R. W. Mar	"Thermochemical Energy Storage and Transport Program Overview"	Second Annual Thermal Energy Storage Contractor's Information Exchange Meeting, Gatlinburg, Tenn.

	Project	O	N	D	J	F	M	A	M	J	J	A	S
1.1.1	Extended Storage for Solar (RRC)	8											
1.1.4	Ammonium Hydrogen Sulfate Decomposition (UH)					5, 6			7	8			
1.1.5	$Ca(OH)_2/CaO$ Reaction (AI)				1, 2			3	4, 5	6, 7, 8			
1.1.6	High-Temperature CHP and Storage Analysis (LBL)	8											
2.1.1	Open Heat Pipe Feasibility (IGT)				4		6	7, 8					
2.2.1	Chemical Heat Pipe Feasibility (GE)	8											
2.2.2	Duplex Steam Reformer (GE)	8											
2.2.3	Alternate Catalyst (GE)	8											
2.2.4	CH_4/H_2O CHP Solar Interface Study (UH)			4, 5, 6					7		8		
2.3.1	Benzene/Cyclohexane Heat Pipe (GE)										1, 2, 3		4
3.1.1	H_2SO_4 Dilution (RRC)	8											
3.1.2	MeOH Based Heat Pump Storage (EIC)			5, 6				7, 8					
3.1.3	Hydrated Salt Heat Pump Storage (CES)	8		9		2, 3, 4		5, 6			7, 8		
4.1	Experimental Heat Transfer Studies (CSU)					7, 8							
4.2	Thermal Decomposition Kinetics (UCD)						5, 6				7, 8		
4.3	SO_2/SO_3 Catalyst Development (RRC)				6			7, 8					
4.4	Ammoniated Chloride Salts (MM)		6				7, 8						

Legend:
1 - Work statement requested
2 - Work statement received
3 - Work statement reviewed
4 - Work statement revised
5 - Work statement accepted
6 - Procurement initiated
7 - Procurement completed; contract awarded
8 - Work in progress
9 - Current contract ends

Figure 14. FY77 Procurement Status

FUTURE ACTIVITIES

Program Planning (WBS 1.1)

Interactions with STOR regarding future direction of TEST program will continue. A draft of the FY 79 Annual Operating Plan will be prepared for submission in May 1978.

Project Review and Evaluation (WBS 1.2)

The report or formal program reviews which are scheduled are so indicated in Figure 15.

Program Administration (WBS 1.3)

Weekly and bimonthly status reports and financial data will be provided to STOR as required.

Procurement (1.4)

Awards of the following contracts are anticipated:

Project No.	Contractor	Date
1.1.5	Atomics International	3/78
1.1.6	Lawrence Berkeley Laboratory	12/77
1.2.1	Gilbert Associates	3/78
2.3.1	General Electric/CRD	3/78
3.1.1	Rocket Research	1/78
3.1.2	EIC	3/78
3.1.3	CES	2/78
4.4	Martin-Marietta	3/78

	PROJECT	O	N	D	J	F	M	A	M	J	J	A	S
1.1.1	EXTENDED STORAGE FOR SOLAR (RRC)												
1.1.4	AMMONIUM HYDROGEN SULFATE DECOMPOSITION (UH)				●								
1.1.5	$Ca(OH)_2/CaO$ REACTION (AI)				●▲								
1.1.6	HIGH-TEMPERATURE CHP & STORAGE ANALYSIS (LBL)		●			●							
2.1.1	OPEN HEAT PIPE FEASIBILITY (IGT)			▲		▲●							
2.2.1	CHEMICAL HEAT PIPE FEASIBILITY (GE)	▲				▲	●						
2.2.2	DUPLEX STEAM REFORMER (GE)			●			●						
2.2.4	CH_4/H_2O CHP SOLAR INTERFACE STUDY (UH)				●								
2.3.1	BENZENE/CYCLOHEXANE HEAT PIPE (GE)												
3.1.1	H_2SO_4 DILUTION (RRC)		●		● ▲								
3.1.2	MeOH BASED HEAT PUMP STORAGE (EIC)			●									
3.1.3	HYDRATED SALT HEAT PUMP STORAGE (CES)			●	▲								
3.1.4	AMMONIATED SALT HEAT PUMP STORAGE (MM)												
4.1	EXPERIMENTAL HEAT TRANSFER STUDIES (CSU)	▲											
4.2	THERMAL DECOMPOSITION KINETICS (UCD)				●								
4.3	SO_2/SO_3 CATALYST DEVELOPMENT (RRC)												
4.4	AMMONIATED CHLORIDE SALTS (MM)	▲			▲								

▲ – REPORT REVIEW
● – PROGRAM REVIEW

Figure 15. Subcontract Reviews

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